# Clays and bacteria carry important role to release Hg from small scale Au mine near Lake Victoria, Tanzania

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> Abstract : Pollution of Hg has attracted much attention in Au mines at North America, Africa, and South America, because Minamata-diseases are still increasing in the 21st century. Mercury fragments influence on not only human but also air and soil environments including natural microbial systems. Studies on bacterial mineralization have received much attention as well. However, only few studies have been conducted on the Au mine in relation to the long-term bioremediation study. In this study, mineralogical properties of clay minerals, goethite, quartz, and calcite associated with heavy metals, such as Fe, Au, Ag, Hg, Ba, Sb, and Pb from the small-scale Au mine, Geita, near Lake Victoria, Tanzania, have been studied using electron micro techniques. The lateritic reddish mud samples were collected from 7 locations of Hg panning ponds whereas air dusts were collected from 35 locations from Dar Es Salaam to Geita for about 1000 km away. Both the wet mud and air dust samples are mainly composed of clay minerals (smectite, halloysite, kaolinite), calcite, and goethite, associated with ppb ordered Hg on the surface or the structures. Observation of FE-TEM electron microscopy and elemental distribution maps revealed that the clay particles, calcite grains, and bacterial colonies contain relatively high Hg and Fe on the surface and/or the structures, indicating Hg pollution release from the panning ponds in the Au mine after heating treatment of Au-Hg amalgam. Volatilization of Hg carry to the air dusts associated with dried fine clays at all over the land in Tanzania. The highest Hg content in the dust was about 7785 ppb in Muguli, Southern parts of Lake Victoria. The soils near Hg panning pond contains relatively high Hg as 1576 ppb in Muhama and 1183 ppb in Rwamagaza. The results suggest that biodegradation of heavy metals by microorganisms associated with clays is one of the primary ways by which heavy metals are eliminated from contaminated sites. The finding of heavy metals-degrading bacteria and clay minerals in the Au

mine may have a significant effect on the weathering processes during the long-term bioremediation in Tanzania.

**Keywords :** Au mine, Hg pollution, panning ponds, air dusts, soils, clay minerals, heavy metalsdegrading bacteria, bioremediation

## Introduction

Concern regarding mercury (Hg) as an environmental contaminant has recently come to the forefront of public awareness. Because of this, many involved in Hg research are being increasingly called upon to help understand the sources and sinks for Hg in the environment, Hg biogeochemical cycle, and the implications for human and ecological health. "Mercury: Sources, Measurements, Cycles and Effects", was published the book by Parsons and Percival (2005) on this timely topic. Mercury is known to have detrimental effects on human health, so it is surprising to read that it may not be worthwhile to regulate mercury release from U.S. power plants. Hg pollution in Au mine has attracted much attention in Africa, North America, and South America because Minamata-diseases are still increasing in the 21st century. Mercury is considered a global pollutant because it is present as gaseous phases, rendering the atmosphere an important pathway by which it can cross national and international boundaries as well as oceans. Mercury contamination associated with small-scale gold mining and processing represents a major environmental and human health concern in Eastern and Southern Africa. Approximately 200,000 - 300,000 persons are involved in small-scale gold mining activities in Tanzania and >200,000 persons in Zimbabwe. Mercury is used mainly for the processing of primary gold quartz veins and supergene gold mineralizations. Gravimetric material flow analyses show that 70-80% of the Hg is lost to atmosphere during processing, 20-30% are lost to tailings, soils, stream sediments and water. For every 1g Au produced, 1.2-1.5g Hg is lost to the environment (van Straaten 2000). Urinary mercury levels in gold mine workers frequently exposed to Hg vapor in amalgamation and burning of amalgam were significantly higher (mean: 241 ng/ ml) than those in the general mine population not occupational exposed to Hg (mean: 2.6 ng/ml) (Ikingura and Akagi 1996).

Similarly, although chelating therapy may remove methyl- and ethyl mercury, it cannot reverse central nervous system damage, implying that prenatal mercury exposure leads to lifelong lost benefits, irrespective of money spent on removing the causal agent from the body after the damage has been done (Zeller and Boot 2005). In Africa, mercury pollution of aquatic ecosystems can potentially be devastating, because there is both high dependence on untreated water and relatively few regulatory controls for monitoring and mitigating aquatic contaminants (Campbell *et al.* 2003). Monitoring of environmental and human exposure to mercury in the Nungwe Bay area of the Lake Victoria goldfields, Tanzania, has revealed low mercury concentrations in fish (range : 1.8 - 16.9 ppb, mean : 7.0 ppb)

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and human hair (range : 156 - 5433 ppb, mean : 947 ppb) that represent background levels. Gold mining has not produced a significant increase in environmental methylmercury that is available for bioaccumulation in aquatic food chains (Ikingura and Akagi 1996, 2003; Machiwa 2004).

Mercury fragments influence on not only human but also air and soil environments including natural microbial systems. Studies on bacterial mineralization have received much attention as well. The biodegradation of heavy metals by microorganisms is one of the primary way by which Hg is eliminated from contaminated sites (Compeau 1985 ; Hughes and Poole 1989, 1991). In general, heavy metal contamination, no matter of their sizes, influence natural microbial system around environments. Many approaches to heavy metal contamination clean up attempted to accelerate natural biodegradation processes in promoting the activity of heavy metal-degrading microorganisms. This is an important perspective to present given the evolving nature of Hg biogeochemistry. The characteristics facilitate the movement of Hg between air, soil, water, and biota, making the biogeochemical cycle extremely complex. While the limitations and uncertainties associated with the development of the Hg biogeochemical cycle create a field of research. Clays and microorganisms are ubiquitous on the Earth's surface and, more often than not, are closely associated with one another. Indeed, microorganisms in soil tend to gather at or near clay surfaces as these are enriched in ions, water, and organic matter relative to the bulk soil. However, only few studies have been conducted both on the panning ponds and air dusts in relation to the long-term bioremediation study.

In this work, we repot the results of a mineralogical and biological investigation of samples from ppb-ordered Hg contaminated panning ponds, soils, and air dusts in Tanzania. In addition, the Au and Hg associated with nm-order mineral grains and bacteria were evaluated in comparison with the indigenous microorganisms using Field Emission microscopy equipped with STEM of Energy selection elemental mapping-TEM. We showed that the Hg-clay nm-crystals were made up of an Au-rich panning pond with bacteria. To our knowledge, there are no previous reports on the natural bioremediation of Au and Hg bioremediation in Au mine in Tanzania.

### **Geological setting**

Precambrian rocks underlie most of central and western Tanzania. Archean granite and greenstone rock assemblages from the central nucleus of the country, the Tanzania Craton, distributed at southern part of Lake Victoria. The Tanzania Craton surrounded by Proterozoic belts : the Palaeoproterozoic Usagaran-Ubendian belt, and the Mesoproterozoic Kibaran (Karagwe-Akolean). The name Lake Victoria Gold Fields (LVGF) refers collectively to a number of gold fields located to the south and east of Lake Victoria in northern Tanzania. Included in the LVGF are the South West Mwanza (Sukumaland) gold field to the south of Lake Victoria, the Musoma gold field to the east of the lake and the Iramba-Sekenke gold field to the south east of the lake. These gold fields occur in Archean (>2400 ma) terrane of weakly metamorphosed mafic and felsic volcanic rocks and graywackes. The terrain belongs to the Nyanzian greenstone belt of Tanzania Craton.

Gold occur in four types of deposits namely : 1, auriferous quartz reefs and stockworks 2, disseminated gold associated with sulphides in banded iron formation (BIF) and sheared metavolcanic rocks (sulphide impregnated deposits) 3, alluvial gold in laterites, and 4, placer gold in river sediments. The first three are by far the most important in terms of grade tenor and spatial distribution. All the important auriferous reefs are associated with major shear zones within the greenstone belt (van Straaten 2000).

Lake Victoria Gold Fields is one of the major producers in the country. The gold production is at both small and large scales. Mercury pollution is dominant in small-scale gold mines and it needs through environmental studies in order to understand the extent of the problem and the control of the use of mercury. The research problem has been clearly identified. Briefly the problem deals with Hg toxicity to human beings. It highlights bioaccumulation by fish, which affects human beings of which the pathways and speciation of Hg in the ecosystem to affect the people is not yet adequately determined.

### Materials and methods

### Field sites and sample collection

The 30 locations studied on the heavy metals-contaminated air dusts and soils in Tanzania (Fig. 1, Table 1). Heavy metal contaminated soils were collected from 6 panning ponds at Geita City, Southern Lake Victoria, on June 2005 (Fig. 2). The field work carry on dry season, therefore the environmental conditions in Tanzania were very dusty throughout the country (Fig. 3). Panning pond water and river water quality near smallscale Au mine at Geita City was performed at 6 locations (Fig. 4, Table 2). Measurements of characteristics of the waters (pH, Eh, EC, Water Temperature and Dissolved Oxygen) in the field are summarized as shown in Table 2.

### Elemental analysis

Soils and the dusts were analyzed by X-ray fluorescence spectrometer (XRF), immediately after returning from the field. Briefly, water samples from panning pond were acidified with HNO<sub>3</sub>. The samples were air-dried up at room temperature and ground to fine powder for ED-XRF analysis. The powder samples were pressed to make pellet and mounted on the Mylar film. Analysis was carried out by an energy dispersive X-ray fluorescence spectrometer (JEOL JSX-3201), using Rh K $\alpha$ , which operated at an accelerating voltage of 30 kV under a vacuum condition.

### Hg quantitative analysis

The determination of mercury by official method and its improved methods was used for Hg quantitative analysis in this study (Korenaga *et al.* 1987; Yamada and Korenaga 1992). Procedure of mercury quantitative analysis as follows ; Soil samples were analyzed for total mercury by means of the Hydride Generation Atomic Absorption Spectrometry (HG-AAS). On addition of 1 ml of distilled water, 2 ml of 1 : 1 mixture of HNO<sub>3</sub> and HClO<sub>4</sub>, and 1ml of H<sub>2</sub> SO<sub>4</sub> to 0.5 g of soil samples, which were preheated at 200  $^{\circ}$ C for two hours. The solid materials were removed from the extracts by the centrifugal separation. The measurements were carried out for 1 ml of the extracts using the HG-AAS apparatus, HITACHI HG-310.

#### X-ray powder diffraction analysis

The purpose of this study was to elucidate the interaction between minerals and indigenous microorganisms in the Hg panning ponds collected from the Au mines studied by X-ray powder diffraction analysis (XRD; Rigaku RINT1200 X-ray diffract meter). Powder samples were prepared by spreading 2 mg of the suspended clays over a 2.5 cm<sup>2</sup> area of



Fig. 1. Map of the research areas near Lake Victoria, Tanzania. The field work carry on June 2005.

		Hg contents (ppb)						
Location No.		Soil	Dust					
1	Dar Es Salaam	12	25					
2	Morogoro	n.d.						
3	Mtumbatu	6						
4	Kongwa Dodoma	n.d.						
5	Dodoma	7						
6	Kondia	n.d.	n.d.					
7		n.d.						
8	Shingida	n.d.						
9	Shingida	21						
10		n.d.						
11	Nzega	n.d.	32					
12	Nzega	n.d.						
13	Shinyanga	31						
14		3						
15	Mwanza	18						
16	Buhalahala	n.d.	5					
17	Geita	1576						
18	Kalemera	14	15					
19	Serengeti gate	10						
20		n.d.						
21		3						
22		n.d.						
23		n.d.						
24	NCAA tourism area	1						
25	Arusha	30	50					
26	Kilimanjaro	8						
27	Hedadu	2	6					
28		2						
29	Mkata	17						
30		24	9					
		n.d.: not detected						

Table 1. Hg concentrate in soils and dusts of 30 locations in Tanzania.

a glass slide. Relative change in the basal spacing of smectite was measured by EG treatment, and observed using Cu-K $\alpha$  radiation, generated at 40 kV and 30 mA, using a scan speed 2°/min. The powder samples on Mylar films were prepared for analysis by energy dispersive X-ray fluorescence spectroscopy (ED-XRF; JSX-3201), using Rh-K $\alpha$  radiation generated at 30 kV under vacuum. The wt% of each element in a sample was determined on the elements heavier than elemental Na.



Fig. 2. Sampling points of dusts and soils at small-scale Au mines near Lake Victoria, Tanzania, on June 2005. The sampling point No. 6 is mainly studied on mud at panning pond.

#### Electron microscopic techniques

For dust and soil samples were directly set up on the sample stub with carbon double sticky tape, and viewed on a JEOL JSM-5200LV scanning electron microscope. Bacterial cells were fixed with 2.5% (v/v) glutaraldehyde for 24 h at 4  $^{\circ}$ C, mounted on copper specimen grids, allowed to dehydrate at room temperature, and then viewed using a JEOL JEM-2000EX at accelerating voltage of 120 kV and energy-filtering TEM (JEM-2010FEF) at



Fig. 3. Field views of the reddish brown lateritic soils (A) and dusty leaves (B) collected from Muguli (sampling No. 1) on June 24, 2005.

pb) Duict Bomories	river water	7705 panning water	river water	river water	127 separation water	panning water	separation water	- panning water	separation water	sr river water	river water	river water	separation water	- river water	panning water	panning water	separation water	*: filtered water
Hg (p Soil	TIOC		•		114	114		287		117	11/		1102	C011		1576	0/01	
	21.2	26.8	29.6	28.4	21.6	20.4	20.1	•	'	24.2	22.5	19.6	22.1	24.7	20.9	24.6	22.4	
	23	114	54	143	60	37	60	42	12	55	21	42	88	146	42	50	22	
[ ([) <sup>m</sup> a/])	2.0	8.7	4.1	$11.1^{*}$	4.9	3.2	4.8	3.3	0.9	4.6	1.8	3.5	8.0	12.9	3.8	3.6	1.8	
)(mo/Sm)	0.09	0.97	0.34	0.32	0.26	0.47	1.21	1.03	0.31	0.30	0.32	0.40	0.63	0.44	0.27	0.58	0.28	
Eh(mV) E(	189	209	158	97	210	159	201	223	433	274	12	272	220	209	290	287	216	
Hu	6.5	7.5	7.6	10.2	6.4	7.3	4.8	5.5	4.3	7.4	6.9	7.1	8.5	9.1	6.8	7.0	6.5	
Comile No	1-1	1-2	1-3	1-4	2-1	2-2	3-1	3-2	3-3	4-1	4-2	5-1	5-2	5-3	5-4	6-1	6-2	
I ocation	LOCATION	Muguli			Comono	Dallicia		Nyankumbu		Mocomo Divor	INTAGGIITA NIVEL		Durance	NWalliagaza		Muhama	Τνταιτα	
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Table 2. Characteristics of river water, panning pond water, and separation water measured in the field of small-scale Au mine at 6 locations in Tanzania shown in Fig. 2

# Hg-release from Au mine by clays and bacteria



Fig. 4. Panning pond at small-scale Au mines in Muhama (sampling point No. 6). In the pan we can see one small grain of Hg-Au amalgam (B).

the accelerating voltage of 200 kV. Energy dispersive spectroscopy (EDS) was also performed during TEM analysis to evaluate changes in elemental compositions of the soils and dust samples in phosphate buffer at room temperature for 1 h. Dehydrated samples in a graded ethanol series (50, 75, 95, and 100%), mounted on carbon-coated copper stubs, and viewed on a JEOL JSM-5200LV scanning electron microscope.

Farther more, ultra-thin sectioned samples after resinous fixation were cut with an ultra-micro tome, and observed it with nm-scale observations on Formvar and carbon-coated copper grids. The elemental distribution analyses of the samples performed with a Field Emission Electron Microscope equipped with STEM detectors showing elemental mapping of transmission electron microscope images (JEOL JEM-2010FEF). The JEM-



Fig. 5. X-ray powder diffraction patterns of the reddish brown mud sample collected from panning pond at sampling point No. 6.

2010FEF, a state-of-the art analytical electron microscope, is equipped with a 200 kV field emission gun (FEG), an in-column energy filter that allows elemental analysis and chemical analysis of specimens, a scanning TEM image generator (EM-Z90471) and an energy dispersive X-ray spectrometer (EX-340251GT). A combination of high-resolution TEM, scanning TEM, and electron energy-loss spectroscopy is a powerful tool in the study of elemental associations in nm-scale particles. Identification of precipitates associated with bacterial cells was accomplished by selected area electron diffraction (SAED). The TEM is an essential tool in all field of basic nm-science including biotechnology and material science, and finds specific elemental distribution.

# Results

### Sampling points and Hg quantitative analysis of dusts and soils

Map of the 30 sampling points of soils and dusts across in Tanzania between Dar Es Salaam and Lake Victoria are shown in Fig. 1 and Table 1. The specific research areas of small-scale Au mines near Lake Victoria closely are shown in Fig. 2 indicating bar graph of Hg contents in soils and dusts. The Hg contents at the 30 research areas and 6 Au mines list up in Table 1 and 2. Characteristics of river water, panning water, and separation water measured in the field of small-scale mine at 6 locations, Tanzania (Fig. 2, Table 2), showing variety pH of 4.3 - 10.2, relatively high oxidation and high EC (mS/cm) conditions. The water temperature at the panning, separation, and river areas indicated about 20 - 30



Fig. 6. X-ray fluorescence analyses of the reddish brown mud sample collected from panning pond at sampling point No. 6. Water (A) and sediments (B) indicate presence of high S content in the water whereas Al, Si, and Fe elements are due to clay minerals.

°C. The fieldwork carry on dry season on June 24-30, 2005, to collect dust and soil samples at small-scale Au mines near Southern Lake Victoria (Fig. 2). The lateritic reddish mud samples were collected from 6 locations of Hg panning ponds whereas air dusts were collected from 30 locations from Dar Es Salaam to Geita for about 1000 km away. The sampling point No. 6 in Fig. 2 is the typical panning pond to collect sediments and water, showing extremely high Hg contents of 1576 ppb. The highest Hg content in the dust was about 7785 ppb in Muguli. Both soil (30ppb) and dust (50 ppb) samples show high Hg content in Arusha, Southern parts of Lake Victoria (No. 25). The soils near Hg panning pond contains extremely high Hg of 1183 ppb in Rwamagaza. Both mercury emissions and deposition are the highest site of panning pond is in Geita City (No. 6; Muhama, 1576



ppb) (Fig. 2, Table 2). In the pan we can see one small grain of Hg-Au amalgam of less 1 cm in diameter (Fig. 4B).

The analytical data suggested that the concentration of Hg between soil and dust at the same area is correlative conditions. Note that mercury emissions and deposition are high at the urban areas, such as Dar Es Salaam (12 ppb for soil and 25 ppb for dust), Shingida (21 ppb for soil), Shinyanga (31 ppb for soil), Mwanza (18 ppb for soil), Arusha (30 ppb for soil and 50 ppb for dust) and Mkata (17 ppb for soil) are high, suggesting that the Hg release from Au mine to whole lands in Tanzania by wind. Field views of the reddish brown laterite soils (A) and dusty leaves (B) collected at Shingida on July 24, 2005, showing 21 ppb Hg in the soil (Fig. 3).

#### X-ray powder diffraction and X-ray fluorescence analyses of mud from panning pond

X-ray powder diffraction patterns of the reddish brown mud sample collected from panning pond at sampling point No. 6 (Fig. 5) identified as smectite (14.24 Å), kaolinite (7.19 Å), quartz (3.29 Å), and goethite (4.14 Å). The 14.24 Å d-spacing shifted to 16.66 Å after EG treatment indicated presence of smectite. The 3.29, 4.21, and 2.03 Å identified as quartz whereas the 4.14 and 2.62 Å can be identified as goethite as well. The goethite poorly crystallized, showing weak intensities. The reddish brown sediments are character-



Fig. 8. Transmission electron micrographs of ultra thin sectioned mud sample collected from the panning pond at sampling point No. 6, showing zero-loss image and distribution maps of N, P, Ca, Al, Si, Fe, and Au elements. Note that Au are associated with Fe and clay minerals (Al-Si).



Fig. 9. Transmission electron micrographs of thin sectioned living bacteria (A - D), quartz (E), goethite (F), and kaolinite (G) with electron diffraction pattern (inset). High dense materials present on/ in the bacteria suggesting bio-mineral products (C and D).



Fig. 10. Scanning transmission electron micrographs of zero loss images of clay particle (A and B) and calcite grain (C, D, and E), showing Hg distribution maps. Note that clay minerals with 10-12 Å d-spacing and calcite accumulate Hg on the surface or inside structure. The Si content map (E) shows independence from Hg distribution.

istic kaolinite-rich lateritic soils.

X-ray fluorescence analyses of the water (A) was collected from panning pond at sampling point No. 6 (Fig. 6) composed of high S content associated with traces of Na, Mg, Al, Si, K, Ca, and Fe. While the sediment (B) composed of mainly Al, Si, and Fe which the chemical components agreed with clay minerals in lateritic soil using XRD analyses (Fig. 5).

## Optical electron microscopy of mud from panning pond

Optical micrographs and TEM ultra thin section micrographs of the reddish brown mud sample collected from panning pond at sampling point No. 6, show inhabitant of living bacteria with cell wall and EPS (external-cellular polymeric substance) are wrapped in the clay particles (Fig. 7). The size of bacteria ranges from 400 nm to 1  $\mu$ m in diameter. The clay particles are oriented with lattice images of 10-12 Å indicating smectite after dehydration of 14 Å. Both optical light and epifluorescence micrographs showing brown colored clay minerals associated with blue light of coccus type bacteria.

# FE-TEM transmission electron microscopy

Transmission electron micrographs of ultra thin sectioned mud sample collected from the panning pond at sampling point No. 6, showing clay minerals associated with Au nmparticles (Fig. 7, 8). The zero loss image and energy-dispersive X-ray elemental maps showed distribution of N, P, Ca, Al, Si, Fe, and Au elements. The Au and Fe elements are co-related in nm-sized particles made up of an Au-rich mud in the panning pond, and it suggests that the Au electronically influences the catalytic properties of Fe (Fig. 8). STEM-EDX maps of Al and Si composition are located at the clay nm- sized particles around bacteria. The p map shows co-related with clay composition of Al and Si maps. The N and Ca distributions are not so clear relation ship between other elements. The living bacteria with cell structure (A, B) and bio-mineralized bacteria with high dense materials on/in the cell (C, D) can be seen with quartz grain (E), goethite grain (F), and kaolinite particles (G) that the minerals identified by characteristic electron diffraction patterns (Fig. 9). Zero loss image and Hg maps of clay particles indicated with precipitation of Hg on the particle, showing 10-12 Å lattice images (Fig. 10, A, B), where as calcite grain accumulated with Hg on the surface (Fig. 10, C, D). The trace of Si adhesion is on the calcite surface (Fig. 10, E).

Scanning transmission electron micrographs and TEM zero loss images of soils (Fig. 11) and dust (Fig. 12) using energy dispersive X-ray analyses can be identified each grain, as indicating elements and identified minerals. Scanning electron micrograph (A), transmission electron micrograph (B, C, D) of soil sample was collected from panning pond in Muhama (Hg 1576 ppb), identify each grains, such as tube-like halloysite, hexagonal calcite, high dense of iron grain (goethite) and kaolinite/or smectite (Al, Si, and Fe)(Fig. 11). A few granules are found composing pure Au (Fig. 11A, center). Abundant coccus typed bacteria are associated with clays and organic matters (Fig. 11 B). Moreover, heavy metals



Fig. 11. Scanning transmission electron micrographs and TEM zero loss images of soils in panning pond (location No. 6), using energy dispersive X-ray analyses indicating elements and identified minerals. Scanning electron micrograph (A), transmission electron micrograph (B, C, and D) of soil sample was collected from panning pond in Muhama (Hg 1576 ppb). The tube-like halloysite (D), and hexagonal calcite (Ca; in C and D), high dense of iron grain (D; goethite), kaolinite/ or smectite grains (Al, Si, and Fe), and a few granules of pure Au (A, center). Abundant coccus typed bacteria are associated with clays and organic matters (B).



Fig. 12. Scanning transmission electron micrographs, TEM zero loss images, and energy dispersive X-ray analysis of dust sample (location No. 1) was collected from Muguli (Hg 7785 ppb), showing abundant heavy metals, such as Ag (A), Pb and Fe (B), Zr (C), Ba (D), and Ce (E), which are always aggregated with clay particles.

of Ag, Pb, Zr, Ba La, and Ce were found with clays (Al, Si) and quartz (Si) associated with organic materials in the panning pond.

Scanning transmission electron micrographs, TEM zero loss images, and energy dispersive X-ray analyses of dust sample (Hg 7785 ppb), was collected from Muguli, can be identified each grains as indicating elements and minerals in Fig. 12. Abundant heavy metals, such as Ag (A), Pb and Fe (B), Zr (C), Ba (D), and Ce (E), which are always associated with clay particles nm -  $\mu$ m in diameter, suggesting easily release to long distance in Tan-





heating at out door

Fig. 13. Schematic diagram of release Hg from small-scale Au mine in Geita near Lake Victoria, in Tanzania, showing relationships between Au and Hg in panning pond, dusts, and soils. The Hg carries on the surface of clay minerals, calcite, and bacteria.

zania by dry wind (Fig. 12).

Schematic diagram of release Hg from mud panning pond at small-scale Au mine in Geita near Lake Victoria, in Tanzania, showing relationships between Au-Hg amalgam, volatilization of Hg by heating at out door, and produced Hg rich dusts and soils at the small-scale Au mine (Fig. 13). In the mud panning pond living bacteria which are tolerant to Hg and Au carry important role to adhere clay particles to the cell wall by EPS, as shown in TEM micrographs. The results suggest that reason why Hg pollution spread to soils and dusts at whole area in Tanzania.

### Discussions

Environmental impacts and human health risks associated with mercury pollution have prompted numerous studies, worldwide, that are geared to provide better understanding of mercury cycling and bioaccumulation in temperate and tropical ecosystem. In tropical regions, small-scale gold extraction by mercury amalgamation is a major source of mercury pollution. The data on atmospheric mercury pollution are still scarce, in spite of the fact that more than 55 % of mercury used in gold extraction is released to the atmosphere during burning and re-burning of amalgams. In the absence of direct air mercury sampling and measurement equipment, the use of locally available plant species in the assessment and evaluation of air pollution patterns in the gold mining area was described (Ikingura and Akagi 2002). Lichens were selected for the assessment of mercury dispersion in air from point sources related to gold mining activities in Tanzania. Theoretically, mercury should preferentially rain down in areas near to power plants. In this study attempts to determine the fallout by wind flow have proved and clays carry important role to release Hg to large

urban city. A partial explanation for this dichotomy is the process by which elemental mercury becomes methyl mercury by microorganisms. For mercury to get methylated and enter the food web, it must be processed by bacteria, thrive on sulfate, a sulfur compound. This means that dissolved organic matter and sulfur enhance methylation, as do panning waters such as those in the small scale Au mine.

Tailings are local "hot spots" with high concentrations of As, Pb, Cu, and Hg. Lateral and vertical disperson of Hg lost to soils and stream sediments is very limited (laterally < 260 m, vertically < 20 cm). Dispersion of mercury from tailings is low because Hg is transported largely in the elemental, metallic form. Fe-oxide rich laterites and swamps appear to be natural barriers for the dispersion of metals in soils and streams. Ground and surface water quality data indicate very low dispersion rates during the dry season (van Straaten 2000). High-resolution TEM-STEM-EELS study demonstrated the presence of nm-scale graphitic carbon agglomerates host even finer (< 3 nm) particles, some of which appear to be Fe-spinels, with typical soot-like onion-ring structures on the coarser fly ash particles in a Kentucky fly ash. The elemental analysis indicated an association of Hg, possibly in sulfide form, with carbon. Arsenic, Se, Pb, Co, and traces of Ti and Ba are associated with these Fe-rich particles (Hower 2005).

Accumulation of heavy metals requires organic matter burial in sediments, which is largely controlled by the sheltering or preservational effects of clay minerals in the sediments. The bio-formation of magnetite and siderite plays an important role in the cycling of iron and carbon as well as in carbon sequestration in natural environments. Biogenic iron-rich minerals and microbial Fe (III) may also serve as physical indicators of previous biological activities (Kim *et al.* 2005). "Biomineralization" is the process by which living organisms convert ions in solution into solid minerals (Swannel and Head 1994). The process is the result of cellular activities that allow for certain physicochemical changes to occur, as shown in this study. Hong and Fie (2005) describe the characteristics of the minerals associated with gold in the Shewushan supergene gold deposit, China, that is mainly composed of quartz, kaolinite, halloysite, minor illite and goethite. In this study, STM maps of mud in panning pond show that the introduction of Au to Fe improves selectivity, and we believe that the surface of the bimetallic nm-particles will still contain some Au with clay particles (Fig. 8), indicating that the Au electronically influences the catalytic properties of Pd, by reported Enache *et al.* (2006).

Ore samples from five copper sulfide deposits associated with Jurassic ophiolites in the Northern Apennine belt of Italy were found to contain Au, Ag and U (Garuti and Zaccarini 2005). They consist of fine-grained sphalerite (< 20  $\mu$ m) spotted with interstitial patches of quartz and calcite. Locally, sphalerite consists of closely packed spheroide (up to 100  $\mu$ m in diameter) coated with a thin shell of silica, possibly representing replacement of radiolarian shells or bacterial colonies, suggesting post-depositional biogenically driven reworking and clastic accumulation of sulfide debris in topographic lows (epigenesis). The close association of pyrite and siderite places the conditions for the formation of hydromarchite at Eh of -0.2 to -0.4 units and pH between neutral (pH=7) and moderately basic (8< pH< 9), compatible with the submarine environment.

The thematic issue on metals in the environment and mine wastes originated from the MAC-sponsored Metal in the Environment symposium and the Environmental Studies of Mine Wastes session held at the GAC-MAC-SEG Annual Meeting in 2003. In this special issue, Sidenko and Sherriff (2005) describe the mineralogical changes that occur in mine wastes following their uncontrolled disposal in the paper entitled "Geochemical and mineralogical zoning of high-sulfide mine-waste at the Berikul mine-site, Kemerovo region, Russia". The composition and nature of the iron oxides in mine wastes from the giant gold mine in Yellowknife, Northwest Territories in Canada, determined that maghemite and hematite contain both As<sup>5+</sup> and As<sup>3+</sup> species (Walker *et al.* 2005). The persistence of As<sup>3+</sup> in roaster-derived maghemite in shallow oxidized shoreline tailings for over 50 years suggests that the arsenic is relatively stable under these conditions, even though As<sup>3+</sup> is a reduced form of arsenic, and maghemite is normally considered a metastable phase.

Siderophres are low molecular weight organic ligands produced by microorganisms and some plants under Fe-limited conditions, and commonly present in soil systems. Siderophores have a high specificity for Fe (III), relative to Fe(II); siderophore Fe (III) 1 : 1 complex stability constants range from 10<sup>23</sup> to 10<sup>52</sup>. Siderophores can also form stable complexes with other metals, such as Al(III), Ga (III), In (III), Cd (II) and Pb (III). This ability to form stable metal-ligand complexes suggests that siderophores may influence metal mobility in soils by affecting rates of mineral weathering (Hepinstall *et. al.* 2005). According Fig.7-12 in this study, potential co-adsorption of siderophore-metal complexes to the mineral-surface might enhance metal adsorption, such as Au, Fe, Hg, As and S. In panning pond sulfur bacterial surface might enhance metal adsorption of Au, Hg, and Fe. Furthermore, cohesion materials on the bacterial surface effects on Au, Fe, and Hg adsorption to clay minerals (smectite, mica clay minerals, and kaolinite). Kim et al (2005) reported the effect of microbial Fe (III) reduction on smectite flocculation.

However, very little is known about the biodegradation of Au, Ag, Hg, and As etc., because of their complex structures, which are difficult to analyze nm-order scale. There is recent evidence of As degradation in hot springs (Tazaki *et al.* 2003, 2004; Ohnuki *et al.* 2004). The mechanism of uptake of arsenic (As) in bacterial microhabitat, a biomat, from discharged arsenic mine water at pH 4.7 in field (As mine in Gunma, Japan) and laboratory experiments. Especially iron bacteria of gallionella sp. was the predominant microorganism present in the biomat, accelerate the oxidation of Fe (II). The uptake of heavy metals concurred with the oxidation of Fe (II) to Fe (III).

Some heavy ions, particularly low-molecular-weight fractions, can also be biodegraded at low concentrations. Korenaga *et al.* (1987) reported that elimination of interference by iodide in determination of mercury by cold-vapor AAS. Further research is still needed to understand the biodegradation of Au, Ag, and Hg compounds. In order to evaluate the potential influence of Fe-cycle bacteria on Fe cycling during post-deposition clayweathering alteration, Fe (III)-reducing and/or Fe(II)-oxidizing microorganisms were examined in open-pit, subsurface mine samples from kaolin lenses and smectite formations collected from sites in central Georgia (Shelobolina *et al.* 2005). All clay samples showed greater numbers of Fe (II)-oxidizing bacteria (22-22 000 cells/g) than Fe (III)-reducing bacteria (3-410 cells/g) as determined by MPN analysis. Anaerobic bacteria involved in both oxidation and reduction of Fe exist in these subsurface clay formations. Crystallization carried out near room temperature or by the slow cooling or slow evaporation of a diluted solution (McCrone 1954). Kim *et al.* (2006) reported the investigation of changes in flocculation properties of Fe-rich smectite suspensions, including settling velocity, aggregate and floc architecture associated with microbial Fe (III)-reduction in the smectite structure. The increased net negative charge caused by microbial Fe (III) reduction significantly promoted clay flocculation by increasing the electrochemical attraction in the smectite suspensions.

In this study, the high concentration Hg in soils, dusts, and panning ponds in small scale mine in Tanzania. The nm-ordered studies suggest that clay minerals and minerals (smectite, kaolinite, quartz, and goethite) reacted with microorganisms. Several anaerobic species may be used to bioremediate Hg and Au organic pollutants either individually or in combination. It is also possible, however, that the indigenous microorganisms inhabiting the panning ponds which are being exposed to heavy metals may also become resistant to or capable of transforming and detoxifying heavy. The presence of miscellaneous pollutants may present extreme challenges to the maintenance of a phylogenetically and functionally diverse microbial community (Shi *et al.* 2002). Here, we show biological and clay-geo-chemical evidence for an increase in heavy metal deposition in small-scale Au mine in Tanzania. Today most clay minerals originate in biologically active soils (Tazaki 2005). Multiple enzymes produce fatty acids in cells, and carry out these bio-chemical syntheses. Hanczyc *et al.* (2003) reported that montmorillonite catalyzes the polymerization of RNA from activated ribosome mucleotide and that montmorillonite accelerates the spontaneous conversion of fatty acid micelles into vesicles.

### Conclusion

This is an important perspective to present given the evolving nature of Hg biogeochemistry. The characteristics facilitate the movement of Hg between air, soil, water, and biota, making the biogeochemical cycle extremely complex. While the limitations and uncertainties associated with the development of the Hg biogeochemical cycle create a field of research. Mercury fragments influence on not only human but also air and soil environments including natural microbial systems. Studies on bacterial mineralization have been conducted on the small scale Au mines in Tanzania. Mineralogical properties of clay minerals, goethite, quartz, and calcite associated with heavy metals, such as Fe, Au, Ag, Hg, Ba, Sb, and Pb from the small scale Au mine, Geita, near Lake Victoria, Tanzania, have been observed using electron micro techniques. The laterite soils of reddish brown mud

samples were collected from 6 locations of Hg panning ponds whereas air dried dusts were collected from 30 locations from Dar Es Salaam to Geita for about 1000 km away. Both the wet mud and air dust samples are mainly composed of clay minerals (smectite, halloysite, kaolinite), calcite, and goethite, associated with ppb ordered Hg on the surface or the structures. Observation of FE-TEM electron microscopy and elemental distribution maps revealed that the clay particles, calcite grains, and bacterial colonies contain relatively high Hg and Fe on the surface and/or the structures, indicating Hg pollution release from the panning ponds in the Au mine after heating treatment of Au-Hg amalgam. Volatilization of Hg carry to the air dusts associated with dried fine clays at all over the land in Tanzania. The highest Hg content in the dust was about 7785 ppb in Muguli, Southern parts of Lake Victoria. The soils near Hg panning pond contains the highest Hg as 1576 ppb in Muhama. The biodegradation of heavy metals by microorganisms is one of the primary ways by which heavy metals are eliminated from contaminated sites, such as in panning pond bacterial surface might enhance metal adsorption of Au, Hg, and Fe. Cohesions of the bacterial cells might be effect on Au, Fe, and Hg adsorption to clay minerals (smectite, mica clay minerals, and kaolinite).

The finding of heavy metals-degrading bacteria had stuck to the clay minerals in the Au mine, where clay may be less of a problem, and may have a significant effect on the processes during the long-term bioremediation. Bacteria use diverse small molecules for extra- and intracellular signaling. Identifying significant sources and sinks of Hg is important for the recognition of global biogeochemical cycles. The primary concern for human health is methyl Hg in aquatic systems, exposure through lateritic dust of clays to local, regional, and global ecosystems.

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