Bull Environ Contam Toxicol (2011) 86:484–489
DOI 10.1007/s00128-011-0242-y

Multielemental Analysis of Migori (Southwest, Kenya) Artisanal Gold Mine Ores and Sediments by EDX-ray Fluorescence Technique: Implications of Occupational Exposure and Environmental Impact

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Received: 28 October 2010 / Accepted: 8 March 2011 / Published online: 20 March 2011

Abstract The results of heavy element profiling of the gold ores and sediments associated with the artisanal gold mining activities of the Migori gold belt of Southwestern Nyanza, Kenya, were reported in this paper. The analysis was made to assess the occupational exposure of the miners as well as to investigate the environmental impact of toxic heavy metals. Gold ores and sediments from the artisanal gold processing were sampled in four artisanal gold mining areas: Osiri A, Osiri B, Mikei and Macalder (Makalda) and analyzed for heavy elemental content using ^{109}Cd radioisotope excited EDXRF spectrometry technique. Analysis consisted of direct irradiating of sample pellets. The concentrations of major elements detected were: titanium (711.41–10,766.67 mg/kg); cobalt (82.65–1,010.00 mg/kg); zinc (29.90–63,210 mg/kg); arsenic (29.30–8,246.59 mg/kg); gold (14.07–73.48 mg/kg); lead (16.31–14,999.40 mg/kg) and mercury (16.10–149.93 mg/kg). The average concentration of the heavy toxic metals i.e. arsenic, lead, titanium and zinc were found to be above 50 mg/Kg as recommended by World Health Organization.

Keywords EDXRF · Toxic heavy metals · Gold mining · Ores and sediments

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The Migori gold mining complex, also referred to as the Migori segment, is part of the Archean Nyanza greenstone belt containing central, proximal and distal facies (Fig. 1). These rocks from the Migori Group consist of the Macalder and Lolgorien subgroups. The mineral potential of the Migori segment revolves around massive sulphide deposits in close proximity to the Macalder and Lolgorien volcanic centers and gold mineralization throughout the belt. Gold has been mined from the small deposits throughout the gold belt from cross cutting quartz veins, banded iron formations, stratabound horizons in tuff, and alluvial and eluvial deposits. Gold was discovered in this region in 1920s where the major mining areas included Macalder, Osiri, Mikei and Masara. By the time major mining operations ceased in 1966 a total of 4,248 kg of gold, 1,210 kg of silver and 20,000 tones of copper had been recovered from the belt (Ogola et al. 2002). After large scale mining stopped artisan mining has been the main source of gold in the region. Artisanal gold mining involves extraction of ore manually from open pits which is then left to dry before crushing into fine grains using mallets. Gold is then recovered from the grains by mercury amalgamation. During artisanal gold mining the size reduction process like crushing increases the surface area of the reaction between rock/mineral particles thereby accelerating oxidation and/or chemical weathering and hence the immobilization of metals and radionuclides to the environment. At low concentrations, some of the metals are essential to plants, animals and humans but at above recommended levels they can be toxic.

Environmental devastation from a number of studies conducted in gold mining areas e.g. the Witwatersrand have produced increasing evidence that mines frequently contaminate adjacent environments with heavy metals, salts and radionucides. In cases where nearby streams are

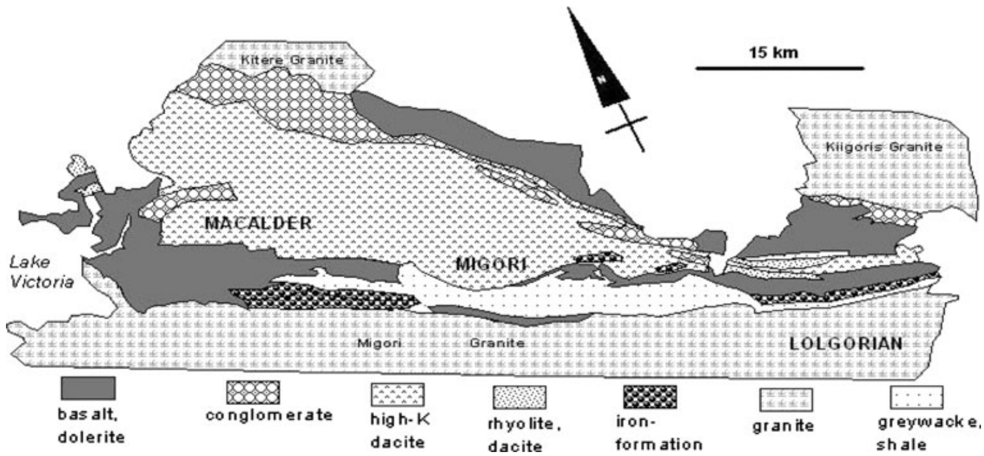

Fig. 1 The Geology of Migori segment Gold mining complex (Ichangi and Maclean 1991)

affected, high rates of downstream transportation and the contamination of soil and sediments far away from the source of pollution are possible (Appleton et al. 2001; Pestina et al. 1997; Winde and Sandham 2004). Pestina et al. (1997) using atomic absorption spectrometry (AAS) in the stream sediments draining the copper and gold mining areas in southern Brazil recorded 0.067–0.430 mg/kg Hg, 4.5–109.5 mg/kg Pb and 40.9–138 mg/kg Zn. However (Ogola et al. 2002) using the same technique while analyzing for Hg, Pb and As in the sediments in the streams draining the Migori gold mining areas recorded higher values of 6.5–510 mg/kg Pb and 0.46–1,920 mg/kg Hg. Heavy metals are of particular concern for a number of reasons. Firstly they show a tendency to accumulate in the sediments and the soils and are non biodegradable. Secondly, they are ubiquitous in sediments and soil arising from both natural and anthropogenic sources. The pathways of the heavy metals include inheritance from the parent rocks, local and long range atmospheric and fluvial deposits of emissions from dust and mining (Getaneh and Alemayehu 2006).

This study aimed at assessing the occupational exposure of the miners as well investigating the environmental impact of toxic heavy metals from Migori artisanal gold mining areas: Osiri A, Osiri B, Mikei and Macalder (Makalda) using EDXRF spectrometry technique.

Materials and Methods

A total of 23 samples (11 ores and 12 sediments): 6 ores and 6 sediments from Osiri (A and B), 4 sediments from Mikei and 5 ores and 2 sediments from Macalder. The sediments from Mikei and Osiri A were collected from panning ponds situated next to crushing sites while sediments from Osiri B were collected from the river bank where placer gold ore was panned. Three of the ore samples collected from Macalder were from reworked tailings while two were solid ores. The ores and the sediments were crushed into fine dust and then sieved through a 100 micron sieve. Three pellets of diameter 25 mm were pressed from each sample each weighing between 2.5 and 4.8 mg. The pellets were then analyzed using energy dispersive X-ray fluorescence (EDXRF) technique. EDXRF technique offers non destructive and reliable method of multi-elemental analytical technique for a wide variety of materials. However, limitation of this sample analysis method is that fluorescent X-rays can easily be absorbed by the sample itself (self absorption); hence it is required to closely match the sample matrix with the calibration standard in terms of composition. Sample fusion also enhances the XRF measurements technique by minimizing particle size effect but sometimes refractory minerals dissolve slowly and don't give satisfactory fusions.

The EDXRF spectrometer used in this study consisted of ^{109}Cd as the excitation source; Canberra Si(Li) detector, an ORTEC spectroscopy shaping amplifier model 571, ORTEC high voltage supply bias model 475, ORTEC liquid nitrogen monitor and a Canberra multichannel analyzer (S-100) interfaced with a 486 channel personal computer. The crystal is molded in a vacuum tight cryostat of liquid nitrogen maintained at a temperature of 77 K (~ -200°C), which assists in reducing the electronic noise and keeping the lithium atoms in the silicon and the lattice point. The diode is depleted of the charge carriers and in effect it becomes an ionizing chamber. Multichannel analyzer (MCA) measures the heights of the amplitude of different pulses and stores the results in memory counters called channels. The number of times the pulses of the same height range has been detected is accumulated in the corresponding analyzer memory resulting into a pulse height distribution. The pulse height distribution is converted into the X-ray energy spectrum by appropriate MCA calibration. The MCA also includes a microprocessor, which is preprogrammed to perform single data analysis operations (like energy calibration, integration, subtraction of

Table 1 Elemental concentration of ore and sediment from Osiri B (mg/kg)

	Osi-O1	Osi-O2	Osi-O3	Osi-O4	Osi-S1	Osi-S2	Osi-S3	Osi-S4
Element								
Ti	10,767 ± 825	1,589 ± 125	9,090 ± 716	2,475 ± 209	2,803 ± 218	10,633 ± 801	9,280 ± 736	13,000 ± 956
Cr	659 ± 102	158 ± 22	607 ± 99	283 ± 41	268 ± 37	769 ± 104	645 ± 105	811 ± 111
Mn	934 ± 80	670 ± 47	2,973 ± 207	2,255 ± 152	1,028 ± 73	2,880 ± 200	3,140 ± 218	3,820 ± 261
Fe	93,867 ± 6,083	30,518 ± 1,981	90,333 ± 5,863	51,250 ± 3,332	54,333 ± 3,515	110,000 ± 7,127	98,900 ± 6,410	116,000 ± 7,530
Co	736 ± 87	509 ± 57	766 ± 85	752 ± 85	1,010 ± 106	889 ± 93	865 ± 91	872 ± 97
Cu	<40	<40	48 ± 10	45 ± 11	49 ± 12	44 ± 10	47 ± 11	51 ± 2
Zn	104 ± 11	62 ± 7	110 ± 17	58 ± 9	86 ± 11	89 ± 11	83 ± 10	101 ± 12
As	191 ± 14	806 ± 53	105 ± 9	118 ± 10	270 ± 19	229 ± 16	172 ± 13	191 ± 14
Au	20 ± 6	14.07 ± 4.46	<10	17 ± 6	<10	<10	<10	25 ± 6
Hg	<2	<2	<2	<2	<2	<2	<2	<2
Pb	20 ± 4	16 ± 3	22 ± 4	30 ± 5	28 ± 5	23 ± 4	52 ± 5	29 ± 4
Rb	33 ± 3	24 ± 2	37 ± 3	91 ± 7	39 ± 4	22 ± 2	39 ± 3	35 ± 3
Sr	49 ± 4	84 ± 6	87 ± 6	53 ± 4	141 ± 10	58 ± 4	93 ± 6	70 ± 5
Y	19 ± 2	21 ± 2	18 ± 2	28 ± 3	29 ± 3	16 ± 1	16 ± 2	21 ± 2
Zr	211 ± 14	125 ± 9	135 ± 9	239 ± 16	158 ± 11	96 ± 6	130 ± 9	193 ± 13
Nb	34 ± 3	14 ± 1	20 ± 2	21 ± 2	12 ± 2	10 ± 1	16 ± 1	28 ± 2

Key: *O* Ore, *S* Sediment

background etc.), for various qualitative and quantitative information. Each pellet was run for 2,000 s and the spectra collected by the Canberra detector with energy resolution of 195 eV for (Mn-K_{α}) X rays at 5.9 keV. Characteristic X-ray spectra obtained from the samples were evaluated by non-linear least squares fitting using the AXIL-QXAS code.

Results and Discussion

Several elements like Ti, Cr, Mn, Fe, Co, Cu, Zn, As, Au, Pb, Rb, Sr, Y, Zr and Nb exists in various quantities in this region as shown by results from ore and sediment samples from Osiri B, Table 1, a typical spectrum from the EDXRF is as shown, Fig. 2. Titanium, zinc, arsenic, lead, copper, mercury and manganese were detected in all the four mines in Migori gold mining belt (Table 3) and their detection limits are shown, Table 2. Existence of lead, mercury and copper confirms the study conducted by (Ogola et al. 2002) which also found the existence of lead, arsenic and zinc in sediments from the rivers (Kuja and Migori) draining through these mining areas using AAS technique. However, mercury was below detection limit (Table 3) in most of these mines. Macalder registered the highest level of gold in the ore, 73 mg/kg; however generally Mikei showed higher gold levels as recorded in sediments and ores. High level of gold in the sediment at Mikei could have been due to contamination from other sediments since the sediments are accumulated over long periods in the panning ponds before reprocessing. However, it should be noted that no sediment was attached to a particular ore at the time of collection and therefore the efficiency of recovery of gold from the ore can't be judged from the gold found in the sediments.

Mercury, which is used in the amalgamation process, is below detection limit in sediments and ores from most of the mines. However, due to poor processing methods mercury is left in the sediments leading to mercury pollution as have been registered in several countries including Brazil, Ghana, and Peru. This is evident from the levels of mercury in the sediments in Mikei where the amalgamation method is used; the average mercury level is 36.21 ± 7.25 mg/kg, compared to Osiri B where mercury was registered below detection limit. The high density of mercury allows gold mercury amalgam to sink to the bottom of the river while sediment is washed away (Alpers et al. 2005). Absence of mercury at Osiri B ore and sediment samples is because no mercury is used in recovery of gold in placer gold mining. However, it is interesting to note the absence of mercury in the sediments from Osiri A even though it was used in the amalgamation process. This could have been due to the long period over which the sediments had been kept. The high level of mercury registered at Macalder (150 mg/kg) in an ore sample could have been due to contamination from sediments since most of the ores collected were from abandoned mines. The high level of copper, 118,533 mg/kg, registered at Macalder justifies the mining of copper alongside gold and silver during the industrial mining in the early 1930's in the Macalder mines (Sanders 1964).

Arsenic, lead and zinc which are always associated with gold mining (Ferreira da Silva et al. 2004) and are toxic, were present at high levels in all the mines, e.g. the average levels of arsenic, lead and zinc were 3,199 mg/kg, 7,375 mg/kg and 10,268 mg/kg respectively, as had also been reported in South Dakota (May et al. 2001) and at Mansfed, Germany (Wennrich et al. 2004). This raises a lot of concern on the health of the miners working at Macalder

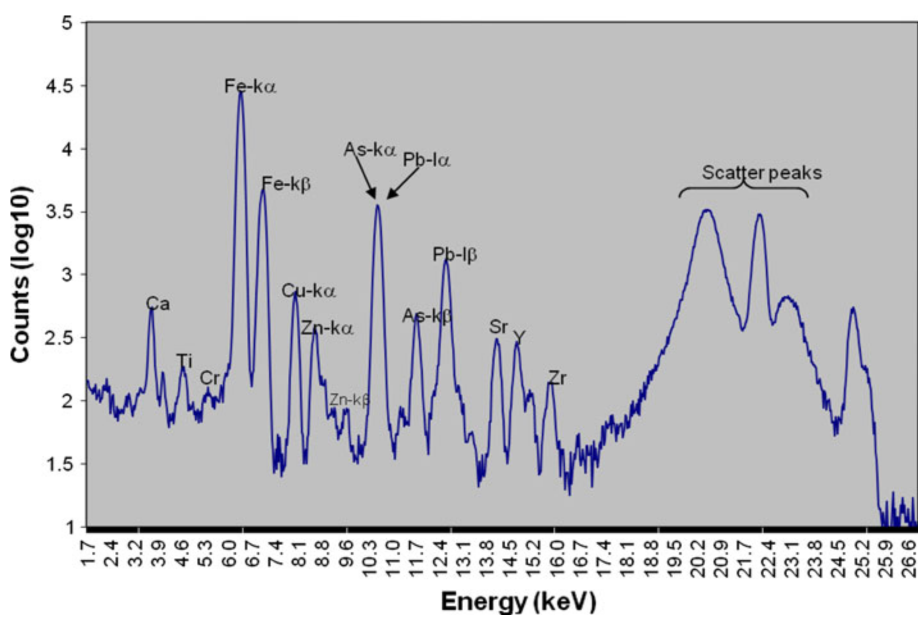

Fig. 2 Typical spectrum from EDXRF, showing energy plotted against counts

Table 2 Detection limits in ores and sediments (mg/kg)

Element	Detection limit
Ti	165
Cr	106
Mn	86
Fe	70
Co	58
Cu	40
Zn	35
As	20
Au	10
Hg	2
Pb	4
Rb	11
Sr	5
Y	4
Zr	4
Nb	3

mines since all the three toxic elements had their highest levels registered at Macalder. These levels are much higher than levels registered in the sediments in ore in Adola regions of Southern Ethiopia which are arsenic 59.7 mg/kg, lead 61.5 mg/kg and zinc 105.5 mg/kg (Getaneh and Alemayehu 2006). The existence of arsenic in the area shows the existence of arsenopyrite which has always presented a problem in the extraction of gold. Arsenic and gold are often related in hard rock gold mines where often gold occurs as tiny blobs within the arsenopyrite. Arsenic is a danger to the miners health and even animals. It is a carcinogen and causes both skin and lung cancer. However, arsenic is used in computing and electronic industries. High levels of zinc, copper, lead and arsenic were reported at Macalder while Osiri B showed high level of titanium in both the sediment and ore.

In conclusion, our study shows that the level of arsenic, copper, lead, and zinc in the Migori gold mines is high and the miners need to take maximum care when mining gold in the region. Extreme care should be taken particularly at Macalder mine where the level of lead, arsenic and zinc is very high. It is further recommended that the miners wash their hands thoroughly after coming from the mining sites to minimize the ingestion of the poisonous metals and if possible wear hand gloves to minimize contact with the

Table 3 Elemental concentration in ores and sediments from Macalder, Mikei, Osiri A and Osiri B in (mg/kg)

Element		Macalder		Mikei		Osiri A		Osiri B	
		Ore	Sediment	Ore	Sediment	Ore	Sediment	Ore	Sediment
Ti	Max	3,690 ± 408	4,123 ± 424	–	4,242 ± 427	7,607 ± 2,384	1,905 ± 192	10,767 ± 825	13,000 ± 956
	Min	2,474 ± 175	3,530 ± 105	–	711 ± 142	2,445 ± 361	1,214 ± 120	1,589 ± 125	2,803 ± 218
	Ave	1,953 ± 201	3,826 ± 106	1,191 ± 216	2,152 ± 235	5,026 ± 1,373	1,560 ± 156	5,980 ± 469	8,929 ± 678
Mn	Max	1,657 ± 128	1,657 ± 107	–	1,019 ± 85	1,517 ± 575	1,263 ± 90	2,973 ± 207	3,820 ± 261
	Min	1,106 ± 93	1,106 ± 102	–	362 ± 34	1,109 ± 91	987 ± 70	670 ± 47	1,028 ± 73
	Av	1,389 ± 109	1,389 ± 105	176 ± 29	564 ± 48	1,313 ± 333	1,125 ± 80	1,708 ± 122	2,717 ± 188
Cu	Max	118,533 ± 7,711	7,443 ± 487	–	303 ± 24	127 ± 49	174 ± 16	48 ± 10	51 ± 2
	Min	1,661 ± 128	5,620 ± 369	–	BDL	BDL	128 ± 14	BDL	44 ± 10
	Ave	27,744 ± 1,811	6,531 ± 428	845 ± 58	174 ± 15	64 ± 25	151 ± 15	23 ± 5	48 ± 9
Zn	Max	63,210 ± 4,103	8,980 ± 586	–	1,227 ± 82	298 ± 118	99 ± 11	110 ± 17	101 ± 12
	Min	1,310 ± 89	6,073 ± 397	–	150 ± 10	98 ± 11	98 ± 10	58 ± 9	83 ± 10
	Ave	10,268 ± 1,189	7,527 ± 492	BDL	586 ± 41	198 ± 65	99 ± 11	84 ± 11	90 ± 11
As	Max	8,427 ± 555	4,310 ± 283	–	5,705 ± 242	881 ± 58	853 ± 57	806 ± 53	270 ± 19
	Min	BDL	2,763 ± 184	–	316 ± 24	29 ± 14	373 ± 26	105 ± 9	172 ± 13
	Ave	3,199 ± 212	3,536 ± 234	222 ± 16	3,274 ± 182	455 ± 36	613 ± 42	305 ± 22	216 ± 16
Au	Max	73 ± 2	BDL	–	73 ± 7	BDL	25 ± 7	20 ± 6	25 ± 6
	Min	BDL	BDL	–	27 ± 23	BDL	20 ± 6	BDL	BDL
	Ave	15 ± 1	BDL	21 ± 5	44 ± 10	BDL	23 ± 7	13 ± 4	6 ± 2
Hg	Max	150 ± 35	BDL	–	62 ± 7	BDL	BDL	BDL	BDL
	Min	BDL	BDL	–	16 ± 6	BDL	BDL	BDL	BDL
	Ave	30 ± 7	BDL	BDL	36 ± 7	BDL	BDL	BDL	BDL
Pb	Max	14,999 ± 978	3,503 ± 228	–	3,548 ± 231	131 ± 52	305 ± 21	30 ± 5	52 ± 5
	Min	1,552 ± 103	3,137 ± 205	–	109 ± 7	30 ± 5	121 ± 10	16 ± 3	23 ± 4
	Ave	7,375 ± 491	3,320 ± 217	28 ± 4	1,473 ± 97	81 ± 29	213 ± 16	22 ± 4	33 ± 5

BDL Below detection limit

metals. Possibilities of extracting other useful metals like copper, arsenic and titanium alongside gold should be explored. Rehabilitation of the mines by the miners should be a priority after the mining period is over.

Acknowledgments We thank the Department of Physics, University of Nairobi, for funding this research.

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