Metal Fractionating Analysis of Termitaria Soil Samples

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Abstract: *This study sought to explore the possibility of using termitaria sampling as a preliminary step in mineral prospecting. Analysis of soil samples collected from various sections of termitaria indicated elevated levels of iron and titanium compared to samples collected from near the termitaria. Fractionation analysis was carried outtoconfirmthe concentration of iron and titanium in termitaria soil samples obtained from mineralized areas in Kenya. This was done after single step extraction of iron and titanium from soil samples.*

Fractionation analysis results confirmed that the termitaria samples had higher concentration of the two metals than the control samples. For the two metals, the residual fraction had the highest percentage, followed by reducible, then oxidizable and lastly exchangeable fractions respectively. The distribution of titanium in the fractions was as follows $T_iRes>T_iRed>T_iEx>T_iOx$ in all samples.For samples from Kwale the mean concentration of Titanium in an anthill was found to be 12.31 mg/g compared to 14.94 mg/g from direct determination representing 82.40 % recovery.The distribution of iron in the fractions was as follows $F_eRes>F_eRed>F_eEx>F_eOx$ in all samples. For samples from Kwale, the mean concentration of iron in an anthill was found to be 22.58 mg/g compared to 25.3 mg/g from direct determination representing 92.5 % recovery. These results demonstrate the potential for use of termitaria soil sampling in mineral prospecting. The study recommends sampling and analysis of termitariasamples from areas whose mineralization is unknown before using other established methods of prospecting.

Keywords:*Fractionation analysis, Termitaria, mobility*

I. Introduction

Kenya largely remains unexplored for minerals (EPZA, 2005). Mineral resources contributes slightly less than one per cent of the gross domestic product (GDP) but there is tremendous minerals potential that await exploitation (EPZA, 2005). With the growing population, there is need to raise the Kenyan per capita income by looking for new foreign exchange avenues. One such approach is by extensively exploiting the mineral resources the country is endowed with.

Identification and quantification of all chemical species, which make the total concentration of a metal in a sample, is a difficult task. Among the challenges is to ensure that the species remains unchanged throughout the analytical procedure (Sanz-Medel, 1998). Physico-chemical properties such as pH and temperature determine the speciation of an element (Templeton *et al.*, 2000). The need for derivatization of an element prior to separation from the environmental matrix inevitably leads to species transformation (Michalke,2003). Derivatizationa is common practice in speciation of environmental and biological matrices, which are generally dynamic (Szpunar,2000). Concentrations of trace metals are sometimes extremely low to the µg L^{-1} levels. Speciation of such metals requires that these low concentrations be further divided into even smaller fractions (Sanz-Medel, 1998). Analytical techniques required to determine such extremely low concentrations need to be very sensitive to achieve very low detection limits. Another challenge with element speciation involves separation and isolation of chemical species from the sample matrix (Kot and Namiesnik, 2000; Sanz-Medel, 1998). Devising an efficient separation technique to separate species in such low concentrations has also posed a challenge to speciation analysis. It is sometimes more practical to identify groups of species of an element and determine the sum of concentrations of metal in the group (Templeton *et al.*, 2000).

II. Materials and Methods

Study Site, Sample Collection, and Preparation

Sampling for this study was carried out at Kwale and TharakaNithi Counties where iron and titanium are known to occur. At TharakaNithi two locations, Kithiori and Kathwana where iron and titanium dioxidehad been mined on small scale were chosen. Soil samples were collected in non-metallic containers to avoid contamination. Clear, sealable plastic bags were used to store and transport materials that were chipped from the termitaria. The soil samples were oven dried at 110° C for six hours,then large particles including stones and plant remains were removed manually. Dried soil samples were separately pulverized to about 100 µm by use of a disc mill pulveriser. A three-step optimized Community Bureau of Reference (BCR) fractionation procedure proposed by Rauret and co-workers (1999) was applied to the soil samples collected from Kwale, Kathwana and

Kithiori which are mineralized areas in Kenya. Acetic acid (0.11 mol L^{-1}), hydroxylammonium chloride (0.5 mol L^{-1}) and hydrogen peroxide (8.8 mol L^{-1}) with ammonium acetate (1 mol L^{-1}) were used to extract metals associated with exchangeable, reducible and oxidizable fractions respectively. Metals in the residual fraction were extracted using *aqua regia*followed by analysis using a Shimadzu AA6200 Flame atomic absorption spectrophotometer (FAAS). As an internal check on the accuracy of the procedure used, metal concentrations insediment samples digested by *aqua regia*were compared with the sum of the four BCR fractions including *aqua regia*digests of the residual fractions. Determinations were carried out using Atomic Absorption Spectroscopy.

Metal Fractionation

Metal fractionation analysis was done according to the procedure modified from the Standards, Measurement and Testing (SM and T, formerly referred to as the BCR) procedure of the European Union as published by Rauret and coworkers (1999). Application of the procedure was aimed at sequentially dissolving metals soluble in acetic acid (0.11 mol L^{-1}), hydroxyl ammonium chloride (0.5 mol L^{-1}), and hydrogen peroxide (8.8 mol L^{-1}) with ammonium acetate (1.0 mol L^{-1}). These reagents target exchangeable, reducible and oxidizable metal fractions respectively. Non-silicate bound metals associated with the residual fraction was extracted by dissolving them in 3:1 HCl-HNO$_3$ solution (aqua regia).

Exchangeable Metals

Twenty milliliters (20 ml) of acetic acid was added to 0.5 g of soil sample in a clean and dry 50 ml centrifuge tube. The tube was tightly capped and placed on a MS1minishaker and agitated at 180 rpm for 16 hours at room temperature. The extract was separated from the residue by centrifugation (using a Centurion Scientific Ltd centrifuge) at 3000 rpm for 20 minutes. Using of a pipette, the supernatant was carefully withdrawn, placed into a 50 ml volumetric flask and made up to the mark with distilled water. This solution was stored in a polyethylene bottle to beanalyzed. The residue was washed with about 10 ml of distilled water, shaken for 15 minutes then centrifuged. This second supernatant was discarded taking precaution not to discard any solid residue, which was to be used in the next step.

Reducible Fraction

Twenty milliliters (20 ml) ofhydroxyl ammonium chloride was added to the residue from the exchangeable fraction. After shaking the mixture for 16 hours at room temperature, it was centrifuged for 15 minutes to separate supernatant from residue. By using a clean pipette, the supernatant waswithdrawn and placed into a 50 ml volumetric flask. This solution was made up to the mark with distilled water, while the residue was washed, centrifuged and the second supernatant discarded.

Oxidizable Fraction

A sample (10 ml) of Hydrogen peroxide solution wasadded to the residue from the reducible fraction, a little at a time to avoid a violent reaction. After one hour, the reaction mixture was placed in a water bath and evaporated to near dryness at 85 °C.After about one hour, the vessel was removed from the water bath and allowed to cool. 25 ml of acidified ammonium acetate solution was added to the moist residue. The vessel was tightly capped then shaken at 180 rpm for 16 hours,then centrifuged as in the previous sections. The supernatant was collected in a 50 ml volumetric flask and made up to the mark with distilled water. The residue was then washed, centrifuged and the second supernatant discarded.

Residual Fraction

Metals bound to the residual fraction were extracted using 3:1 HCl-HNO$_3$ mixture (aqua regia) according to the ISO Standard 11466 (Rauret*etal.,* 2000). Determination of the two metals in various fractionswas done using FAAS.

III.   Results and Discussion

Fractional Analysis of Iron

From Table 1,the distribution of iron in the fractions was as follows $F_eRes>F_eRed>F_eEx>F_eOx$ in all samples. As in single step extraction, the control sample had the least level of iron metal. For samples from Kwale, the mean concentration of an anthill was found to be 22.58 mg/g compared to 25.3 mg/g representing 89.25 % recovery. For samples from Kathwana, the mean concentration of an anthill was found to be 95.54 mg/g compared to 98.53 mg/g representing 96.97 % recovery. For samples from Kithiori, the mean concentration of an anthill was found to be 80.28 mg/g compared to 89.46 mg/g representing 89.74 % recovery. 61.43% of iron in Kwale samples was in the residual fraction whereas only 5.93 % was in oxidizable fraction. For samples from Kathwana 91.41% of iron was in the residual fraction and only 2.23 % was in the

oxidizablefraction. Residual fraction for samples from Kithiori had 89.46 % iron but only 1.81% was in the oxidizable fraction. Metals associated with the residual fraction are strongly bound to the silicate mineral matrix. (Tokalioglu*et al.*, 2003a). Most of the iron was bound to the residual fraction and therefore is largely immobile

A very small fraction is associated with the exchangeable fraction, while a comparatively larger fraction is associated with the organic. Recovery values for iron were close to 100 %. Recoveries exceeding 100 % are an indicator of possible contamination of sample with that metal, or most probably from error while lower recoveries indicate possible loss of sample during extraction. Iron does not form volatile compounds hence no loss is expected.

Table 1: Concentrations of Iron in Various Fractions in mg/g

		EX	%	RED	%	OX	%	RES	%	TOTAL	Acid digestion extraction	% recovery
Kw	A	1.75±0.09	9.5	5.02±1.11	26.82	1.30±0.18	6.94	10.65±1.16	56.89	18.72	20.63	90.74
	B	1.83±0.17	7.20	5.74±1.13	22.60	1.33±0.20	5.24	16.50±1.17	64.96	25.4	23.63	107
	I	1.85±0.13	7.29	5.55±1.17	21.88	1.36±0.16	5.36	16.0±1.31	63.09	25.36	27.12	93.51
	M	1.95±0.19	8.98	5.08±1.00	23.4	1.34±0.22	6.17	13.34±2.21	61.45	21.71	23.05	94
	T	1.86±0.08	8.56	5.63±1.25	25.90	1.37±0.13	6.30	12.87±1.19	59.23	21.73	24.40	89.05
	Mean	1.85	8.19	5.40	23.91	1.34	5.93	13.87	61.43	22.58	25.3	89.25
Ka	A	1.96±0.12	2.15	3.34±1.10	3.63	1.41±0.11	1.53	85.41±10.9	92.72	92.12	90.53	101.76
	B	2.09±0.14	2.13	4.40±1.04	4.49	1.44±0.24	1.47	90.09±12.8	91.91	98.02	98.51	99.50
	I	2.28±0.13	2.36	5.18±1.14	5.38	1.47±0.13	1.53	87.36±10.3	90.73	96.29	97.90	98.4
	M	2.15±0.11	2.23	5.79±1.10	5.60	1.44±0.15	1.49	87.17±11.0	90.28	96.55	99.13	97.4
	T	2.06±0.10	2.18	4.55±1.21	4.80	1.46±0.20	1.54	86.64±20.7	91.48	94.71	98.56	96.1
	Mean	2.21	2.23	4.65	5.41	1.44	1.51	87.33	91.41	95.54	98.53	96.97
Ki	A	1.18±0.11	1.57	4.26±1.07	5.67	1.43±0.17	1.90	65.28±13.2	86.87	75.15	82.63	87
	B	2.76±0.17	3.47	5.06±1.00	6.36	1.45±0.15	1.82	70.34±14.1	88.36	79.61	86.74	91.78
	I	2.91±0.18	3.53	4.67±1.03	5.66	1.45±0.10	1.76	73.47±13.4	89.05	82.5	93.68	88
	M	2.78±0.14	3.43	4.88±1.13	6.02	1.46±0.16	1.80	71.96±13.7	88.75	81.08	90.24	89.85
	T	2.88±0.13	3.47	5.7±1.00	6.86	1.48±0.14	1.78	72.98±12.5	87.89	83.04	87.18	95.25
	Mean	2.50	3.11	4.91	6.12	1.45	1.81	70.81	88.20	80.28	89.46	89.74

KEY
KWKwale samples
KAKathwana samples
KIKithiori samples
A Sample collected **A**djacent to the anthill (control)
B Sample collected from the **B**ottom of an anthill
ISample collected from the **I**nside of an anthill
M Sample collected from the **M**iddle of an anthill
TSample collected from the **T**op of an anthill
EX Exchangeable fraction
REDReducible fraction
OX Oxidizable fraction
RES Residual fraction

Fractional analysis of Titanium
Table 2gives a summary oftitanium concentration in the various fractions, their percentages and percentage recoveries.

The distribution of titanium in the fractions was as follows $T_iRes > T_iRed > T_i Ex > T_iOx$ in all samples. As in single step extraction, the control samples had the least level of Titanium metal. For samples from Kwale the mean concentration of an anthill was found to be12.31 mg/g compared to 14.94mg/g representing 82.40 % recovery. For samples from Kathwana the mean concentration of an anthill was found to be12.57mg/g compared to14.52 mg /g representing 86.57 % recovery. For samples from Kithiori, the mean concentration of an anthill was found to be14.85 mg/g compared to18.47mg/g representing 80.40 % recovery.

76.36% of titanium in Kwale samples was in the residual fraction whereas only 3.33 % was in oxidizable fraction. For samples from Kathwana 83.69% of titanium was in the residual fraction and only 2.55% was in the oxidizable fraction. Residual fraction for samples from Kithiori had 79.01% titanium but only 3.54% was in the oxidizable fractions.

Table 2: Concentration of Titanium in Various Fractions in mg/g

		EX	%	RED	%	OX	%	RES	%	TOTAL	Acid digestion extraction	% recovery
Kw	A	0.62±0.03	5.94	1.32±0.19	12.67	0.32±0.01	3.07	8.17±1.82	78.33	10.43	14.72	70.09
	B	0.72±0.07	5.31	1.72±0.40	12.69	0.37±0.03	2.73	10.74±0.49	79.26	13.55	15.59	86.91
	I	0.79±0.01	6.40	2.08±0.21	16.84	0.41±0.03	3.32	9.07±0.27	73.44	12.35	15.42	80.00
	M	0.86±0.00	6.89	1.17±0.36	9.38	0.45±0.00	3.61	10.0±0.97	80.13	12.48	13.65	91.43
	T	0.95±0.02	7.45	2.28±0.74	17.87	0.49±0.05	3.84	9.04±1.23	70.85	12.76	15.08	84.62
	Mean	0.79	6.42	1.71	13.89	0.41	3.33	9.40	76.36	12.31	14.94	82.40
Ka	A	0.35±0.01	3.15	1.07±0.32	9.64	0.27±0.06	2.43	9.41±2.17	84.78	11.1	13.13	84.54
	B	0.45±0.01	3.74	1.21±0.50	10.06	0.31±0.04	2.58	10.06±0.78	83.62	12.03	16.9	71.14
	I	0.38±0.03	2.86	1.17±0.08	8.80	0.29±0.09	2.18	10.91±1.14	82.09	13.29	13.38	99.32
	M	0.49±0.07	3.72	1.26±0.33	9.57	0.38±0.01	2.89	11.03±0.07	83.81	13.16	14.29	92.09
	T	0.43±0.02	3.24	1.31±0.39	9.87	0.35±0.05	2.64	11.18±2.05	84.25	13.27	13.5	98.30
	Mean	0.42	3.34	1.20	9.55	0.32	2.55	10.52	83.69	12.57	14.52	86.57
Ki	A	0.56±0.02	4.45	1.49±0.73	11.84	0.46±0.07	3.66	10.07±1.65	80.05	12.58	15.93	78.97
	B	0.65±0.04	4.26	1.75±0.17	11.46	0.49±0.03	3.21	12.38±1.79	81.07	15.27	18.34	83.26
	I	0.78±0.02	5.47	1.92±0.04	13.46	0.47±0.02	3.30	11.09±2.03	77.77	14.26	17.86	79.84
	M	0.67±0.06	4.68	1.90±0.27	13.28	0.55±0.03	3.84	11.19±1.10	78.20	14.31	22.00	65.00
	T	0.98±0.11	6.31	1.87±0.65	12.03	0.58±0.01	3.73	12.11±1.01	77.93	15.54	15.68	99.11
	Mean	0.73	5.07	1.79	12.44	0.51	3.54	11.37	79.01	14.39	18.47	80.40

IV. Conclusions

Fractional analysis results showed low concentration of the two metals in control samples compared to termitaria samples. The distribution of iron in the fractions was as follows:$F_eRes>F_eRed>F_eEx>F_eOx$ in all samples an indication that iron is immobile. The distribution of titanium in the fractions was as follows:$T_iRes>T_iRed>T_i Ex >T_iOx$ in all samples also an indication that titanium is not mobile.

There were elevated levels of the two metals in termitaria soils compared to the surrounding soils. Termites are very important bioturbators and are responsible for the higher levels of the metals in termitaria soil samples having brought debris containing the metals from underground.Termitaria sampling can therefore be used as a preliminary step in mineral prospecting since they provide an indication of the potential of positive ore occurrence, and enables judgment on the scale of the ore metal accumulation.

The higher iron and titanium content of the soils in termite mounds compared with the surroundings confirm previous findings that soils had been transported from deep subsoil with a high content of the underneath material to build the mounds.

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