STUDY ON MAGNETIC PROPERTIES, MINERALOGY AND HEAVY METALS CONTENT OF SOIL AND CONCRETION

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ABSTRACT. *This paper presents the magnetic properties, mineralogy and heavy metals content of soil and concretion samples taken from areas of Kundasang (K-S1 and K-C1) and Ranau (R-S2 and R-C2), Sabah. Samples were extracted by a U-formed magnet with strength of 780 Gauss to isolate the magnetic particles and later characterized using Vibrating Sample Magnetometer (VSM), X-Ray Diffraction (XRD), and Atomic Absorption Spectrometer (AAS) techniques. Magnetic parameters such as saturation magnetization, M_s, remanent magnetization, M_{rs}, coercive force, H_c and coercivity of remanence, H_{cr} were determined from the hysteresis loops measurement at room temperature. Based on ratio of M_{rs}/M_s and H_{cr}/H_c, the soil (K-S1) and concretion (K-C1) from Kundasang were classified as pseudo-single domain (M_{rs}/M_s =0.207; H_{cr}/H_c =1.75) and multi domain (M_{rs}/M_s =0.051; H_{cr}/H_c =1.77) grains, respectively. Whereas, both of Ranau samples, R-S2 (M_{rs}/M_s =0.218; H_{cr}/H_c = 1.07) and concretion, R-C2 (M_{rs}/M_s =0.193; H_{cr}/H_c =0.63) exhibit pseudo-single domain properties. Mineral identification from XRD analysis indicates all samples were matched with diffraction line of hematite (Fe_2O_3) and quartz (SiO_2) minerals. The concentration of heavy metals demonstrated high content of Ni and Cr in concretion of K-C1 (Ni, 3364 ± 41 mgkg^{-1}; Cr, 1126 ± 16 mgkg^{-1}) and in soil of R-S2 (Ni, 2209 ± 71 mgkg^{-1}; Cr, 2221 ± 19 mgkg^{-1}). Concentration of other elements (Zn, Cu, Pb and Cd) were found less than 55 mgkg^{-1}.*

KEYWORDS: concretion, pseudo-single domain, hematite, heavy metals.

INTRODUCTION

Magnetic properties of soil are predominant caused by specific types of iron minerals such as iron oxide, iron-titanium oxide and iron sulphide. Several minerals of iron oxides have magnetic characteristics like goethite, hematite, lepidocrocite, magnetite and maghemite, (Dearing, *et al.*, 1995) and listed in Table 1. Iron containing minerals can be found in igneous rock such as basalt, gabbro, metamorphic and sedimentary rocks. Iron can also be found as laterite iron concretions (LIC) which are natural intergrowth of iron, manganese, titanium and aluminum oxides and hydroxides with admixed quartz grains and clay minerals. It also exists in oxysols that are common in non-arid tropical and subtropical environments and a product of intensive chemical weathering under strong oxidizing conditions (Schellmann, 1994).

According to Petrovsky, *et al.*, (2001) these magnetic minerals can be of lithogenic origin, derived from a parent rock in which the soil was developed, or can be formed *in situ* by pedogenic process. Studies have been carried out to investigate the magnetic mineralogy of soils (Liu *et al.*,

1999; Lu *et al.,* 2008a), correlation of magnetic properties of soil and heavy metal contents (Lu and Bai, 2006; Hu *et al.,* 2007) as indicator for heavy metal contamination, besides the determination of physical properties of magnetic grains such as magnetic anisotropy (Tarling and Hrouda, 1993) and distribution of grain size and shape (Dunlop and Odzemir, 1997).

Day et al., (1977) proposed a graph known as Day Plot which is the ratio of saturation remanence to saturation magnetization M_{rs}/M_s , against the ratio of remanent coercive force to ordinary coercive force H_{cr}/H_c and further developed by Parry (1982) which can be measured from the hysteresis loop. Hysteresis loop is a graph of magnetization (M) against applied magnetic field (H). At low magnetic field, magnetization increases proportionally and the magnetization process is reversible. At higher H, the magnetization is not proportional to H and the curve irreversible, and a small proportion of the M, referred to as the remanent magnetization (M_{rs}), is retained by the material after a field removal. As H increases further, the saturation magnetization (M_s), is reached. If the applied magnetic field increased in the opposite (-*H*), the total magnetization of the sample will fall to zero at the value of -H referred to as the coercive force (H_c). The back field which leaves the sample with zero magnetization is known as the coercivity of remanence (H_{cr}) (Opdyke & Channell, 1996).

The Day Plot has been used in paleomagnetic and environmental magnetic of soils, lake and marine sediment to investigate the changes in magnetic minerology (Odzemir & Banerjee, 1982; Smirnov & Tarduno, 2000). This plot also used in magnetic studies on oceanic rocks (Gee & Kent, 1999) carbonate rocks (Channel & McCabe, 1996) and basalt soils (Lu *et al*., 2008b) to differentiate the domain state for single domain (SD), pseudo-single domain (PSD), multi domain (MD) and by, implication, magnetic minerals grain size.

In this paper, we present the magnetic properties based on the Day Plot, mineral compositions and heavy metals content of soil and concretion samples.

Table 1. Magnetic Properties of Some Minerals

Mineral	Composition	Magnetic Order	Saturation Magnetization M_s (Am^2kg^{-1})
Oxides			
Hematite	α-Fe_2O_3	Antiferromagnetic	0.4
Maghemite	γ-Fe_2O_3	Ferrimagnetic	70-80
Ilmenite	$FeTiO_3$	Antiferromagnetic	
Magnetite	Fe_3O_4	ferrimagnetic	90-92
Sulfides			
Pyrrhotite	Fe_7S_8	Ferrimagnetic	20
Greigite	Fe_3S_4	Ferrimagnetic	~25
Oxyhydroxides			
Goethite	α-FeOOH	Antiferromagnetic	<1
Lepidocrocite	γ-FeOOH	Antiferromagnetic	
Metals			
Cobalt	Co	Ferromagnetic	161
Iron	Fe	Ferromagnetic	218
Nickel	Ni	Ferromagnetic	55

(Source : Hunt *et al*., 1995)

MATERIALS AND METHODS

The concretion and soil samples were taken from nearby Desa Cattle, Kundasang (06° 01' N 116° 35' E) and Kg Tanah Merah, Ranau (05° 58' N 116° 41' E) which originate from ultrabasic area and located about 80 km from Kota Kinabalu, Sabah. Map of the sampling location modified from Jacobson (1970) is shown in Figure 1. Figure 2 (a) and (b) show the concretion sample from Kundasang (K-C1) and Ranau (K-C2) respectively. Magnetic particles were extracted from soil and concretion sample with a U-formed magnet bar with strength of 780 Gauss. Samples were crushed using a mortar before the extraction was done. Magnetization measurement (hysteresis loop) was measured for extracted samples using a Vibrating Sample Magnetometer (VSM) at room temperature (Rivas *et al.,* 2006). Identification of mineralogy was characterized by using X-Ray Diffractometer (Philips PW 3040/60 X'pert Pro) with CuKα radiation (40 kV, 30 mA) with wavelength of 1.5405 Å. The diffraction pattern was recorded from 20°-80° (2-theta). Mineral identification of the magnetic samples was performed using X'Pert Highscore Software with support from ICDD-PDF-2 database. Heavy metal in soils and concretions were extracted by acid digestion method recommended by USEPA (1996) and the concentrations of heavy metals were measured by Atomic Absorption Spectrometer (Model Perkin Elmer 4100).
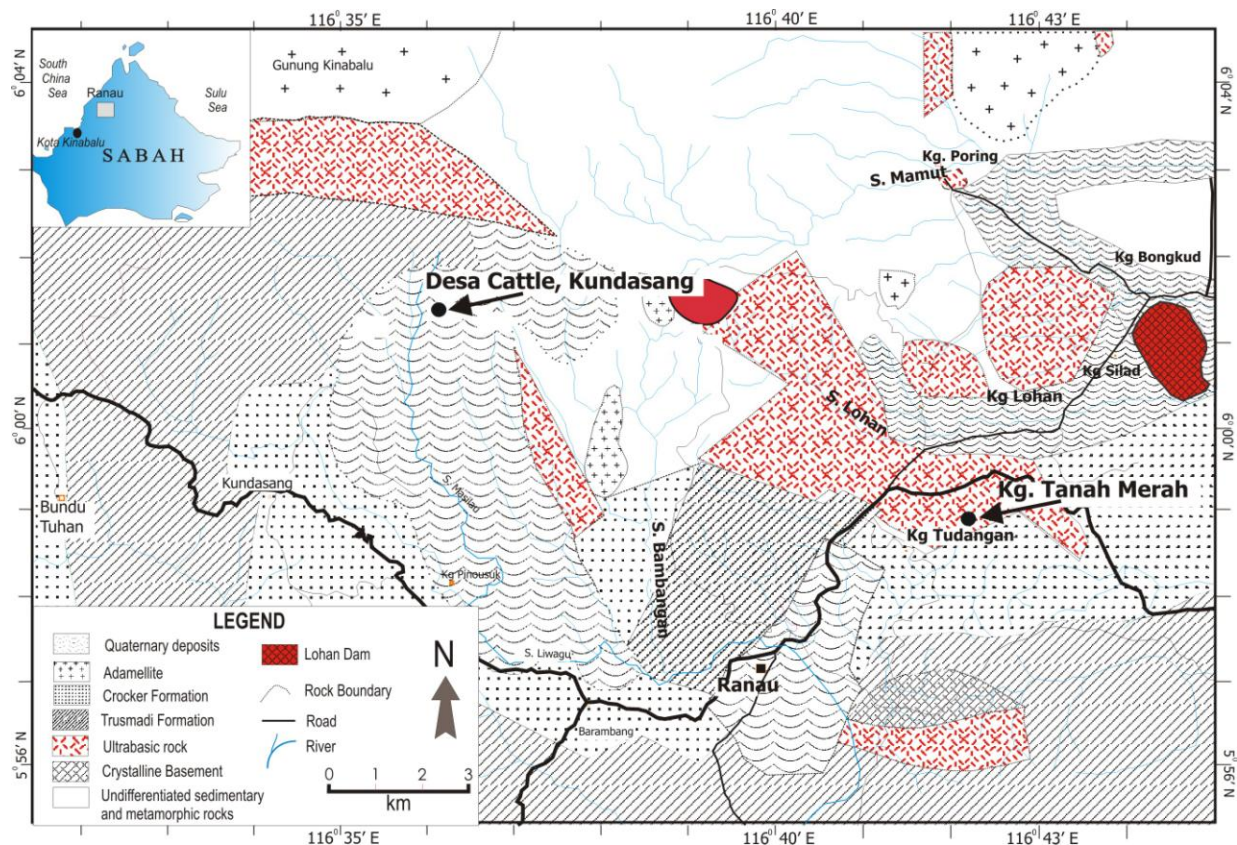

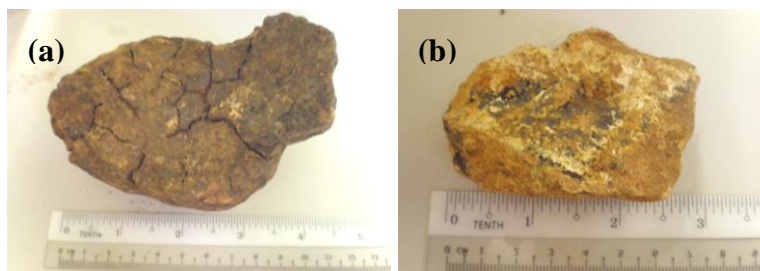**Figure 1. Map of Sampling Location (modified from Jacobson, 1970)**

Figure 2. (a) Concretion Sample (K-C1) from Kundasang. (b) Concretion Sample (R-C2) from Ranau

RESULTS AND DISCUSSIONS

Magnetization measurement

Magnetization (emu/g) versus applied magnetic field (0-2000 Gauss) curves for soil and concretion samples are presented in Figure 3. Table 2 shows the magnetic parameter (M_s, M_{rs}, H_c, and H_{cr}) for each sample, obtained from hysteresis loops. Saturation magnetization, M_s, were calculated by averaging magnetizations measured on the plateau curve, while the remanent magnetization, M_{rs} and coercive force measured at H=0 and M=0 points, respectively (Kosterov, 2001). The coercivity of remanence, H_{cr} was calculated at the back field which leaves the sample with zero remanent magnetization (Opdyke & Channell, 1996).

From the hysteresis loop, soil sample (R-S2) shows the highest saturation magnetization which is 10.394 emu/g compared to the soil from Kundasang (K-S1) with 7.458 emu/g. Sample concretion from Kundasang (K-C1) indicates higher value of saturation magnetization than concretion from Ranau (R-C2) with 4.017 emu/g and 1.280 emu/g, respectively. The difference of saturation magnetization for all samples may result from the different types and composition of magnetic minerals in both soil and concretion. The differences of minerals are shown in Table 3 (XRD analysis). Samples of R-C2 shows high coercive force, H_c (283.46 G) and R-S2 high coercivity of remanence, H_{cr} (202.60 G). The high coercivity may be contributed from effects of antiferomagnetic phases of hematite (Lu *et al*., 2008a) and this was also proved by Tarling (1983) where the presence of hematite was usually accompanied by the presence of a high coercivity. From this study the presence of hematite and magnetite minerals was confirmed in XRD profiles for R-C2 and R-S2 samples as shown in Figure 6.

Hysteresis loop can also provide information about the domain state of ferrimagnetic material, as reported by Dunlop and Ozdemir (1997). From the loops, it can be seen that, samples of K-S1, R-C2 and R-S2 display a wide loop than the K-C1 with a narrow loop. In order to classified the domain state and the grain sizes for each sample, the hysteresis ratio (M_{rs}/M_s versus H_{cr}/H_c) according to the Day Plot is illustrated in Figure 4. The plot shows the samples of K-S1, R-C2 and R-S2 fall within pseudo-single domain (PSD) grains, while the K-C1 falls in multi domain (MD) grains. Following the Day *et al*.(1977), for the single domain (SD), the grain size shall be less than 0.1 μm, while for the multi-domain (MD) the grain is between 15-20 μm, and the intermediate regions between SD and MD are usually referred as a pseudo-single domain (PSD) grain.
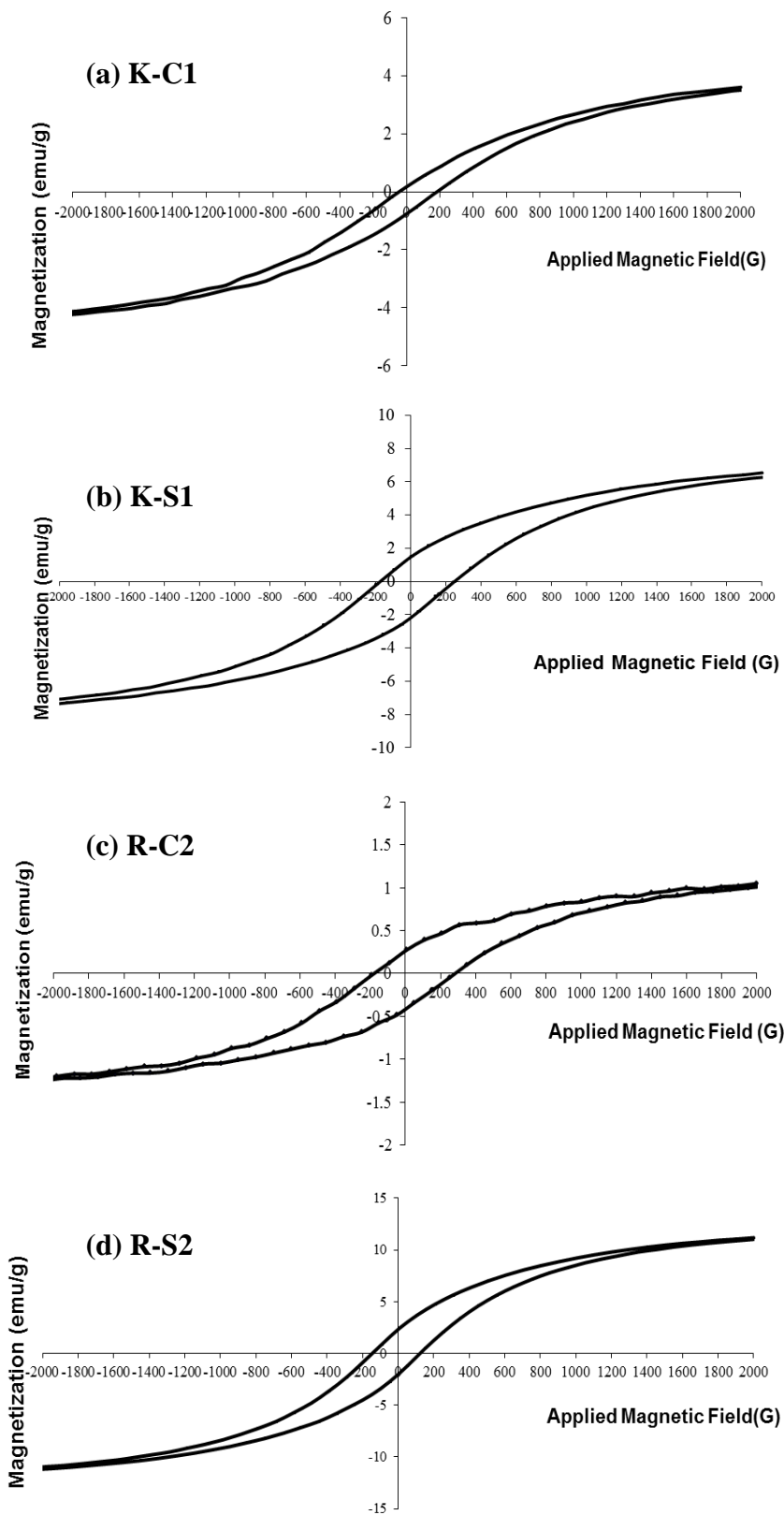
Figure 3. Magnetic hysteresis loops of samples at room temperature

Table 2. Magnetic hysteresis parameters for soil and concretion samples

Sample	H_c (G)	H_{cr} (G)	H_{cr}/H_c	M_s (emu/g)	M_{rs} (emu/g)	M_{rs}/M_s
K-C1	107.79	190.73	1.77	4.017	0.203	0.051
K-S1	108.58	189.96	1.75	7.458	1.544	0.207
R-C2	283.46	177.83	0.63	1.280	0.247	0.193
R-S2	188.57	202.60	1.07	10.394	2.264	0.218

M_s = saturation magnetization; M_{rs} = remanent magnetization; H_c = coercive force; H_{cr} = coercivity of remanence
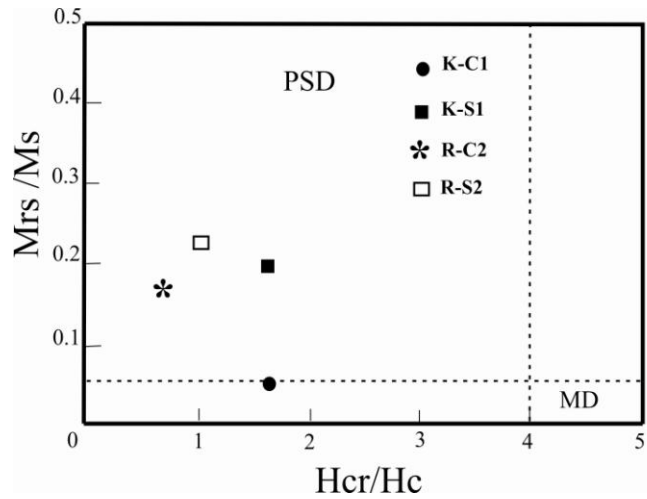

Figure 4. Hysteresis ratio (M_{rs}/M_s versus H_{cr}/H_c) plotted based on a *Day Plot* for all samples. (PSD: pseudo- single domain; MD: multi- domain)

Mineralogy Composition

Minerals composition and XRD profiles of concretions and soils are presented in Table 3, Figure 5 and Figure 6 respectively. It was found that the X-ray diffraction peaks of K-C1, K-S1, R-C2 and R-S2 were matched with the diffraction line of hematite (α-Fe$_2$O$_3$) and quartz (SiO$_2$) minerals from ICDD-PDF-2 database. Hematite presence at 2θ= 35.69^0 in K-C1 and 35.60^0 in K-S1. This mineral is also identified as the predominant phase in samples from Ranau with diffraction angles of 24.45^0 and 35.68^0 in R-C2 as well as 33.34^0 and 35.75^0 in R-S2. Hematite is a common iron oxide found mainly in tropical soil (Alloway, 1995) and their occurrence yield the soil with a reddish colors. This iron oxide mineral was classified as antiferomagnetic minerals (Opdyke & Channell, 1996). Mineral of quartz was presences at diffraction peaks of 21.43^0, 26.68^0 and 36.99^0 in K-S1; 20.89^0, 26.69, 50.15^0 and 54.89^0 in K-C1; 60.18^0 in R-C2; 31.54^0 and 26.67^0 in R-S2. A strong diffraction peak of quartz is observed in a range of 2θ =26.67 to 26.69^0. These quartz mineral is as diamagnetic minerals (Oldfield & Thompson, 1986). In addition, gibbsite and magnetite also exists in soil samples but with low intensity.

Table 3. Minerals Content in the concretion and soil samples using XRD

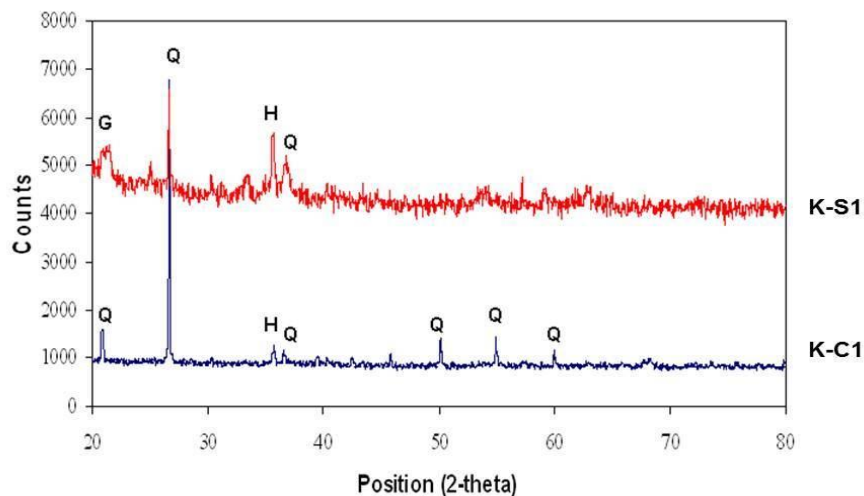| Sample	Minerals
K-C1	Hematite, Quartz
K-S1	Gibbsite,Hematite,Quartz
R-C2	Hematite, Quartz
R-S2	Gibbsite,Hematite,Magnetite,Quartz

Figure 5. X-Ray Diffraction profiles of the concretion (K-C1) and soil (K-S1) samples from Kundasang. (Q-quartz; H-hematite, G-gibbsite)
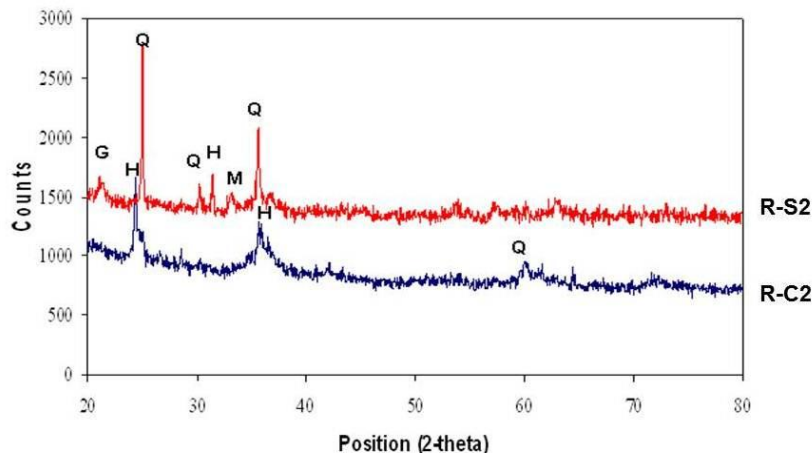
Figure 6. X-Ray Diffraction profiles of the concretion (R-C2) and soil (R-S2) samples from Ranau (Q-quartz; H-hematite, M-magnetite; G-gibbsite)

Heavy Metals Content

The concentrations of heavy metals (Ni, Cr, Zn, Cu, Pb and Cd) are summarized in Table 4. Heavy metals analysis revealed high concentration of Ni and Cr. Concentrations of Ni and Cr in samples from both areas are much higher than other elements. The highest concentration of Ni in K-C1 is 3364.00 mgkg^{-1} and the highest concentration of Cr is 2568.00 mgkg^{-1} in K-S1. Brook (1987) mentioned that both of these elements are more concentrated in ultrabasic soils compared to other elements, as samples are taken from ultrabasic area. Based on study carried out by Sahibin *et al.,* (2009), the concentrations of heavy metals in ultrabasic soils were also found high for in Ni and Cr. Baba *et al*., (2003) mentioned that the high concentration of Cr and Ni in soil from Ranau was due to the leaching process where migrations of heavy metals occurred from the upper to the bottom part of soil profile. Concentrations of Zn and Cu for soil and concretion from Ranau were greater than the samples from Kundasang. Concentration of Zn is 159.17 mgkg^{-1} in R-C1 and 132.25 mgkg^{-1} in R-S1, whereas concentrations of Cu are 54.11 in R-C1 and 49.75 mgkg^{-1} in R-S1. Concentration of Zn for K-C1 and K-S1 were 81.25 mgkg^{-1} and 55 mgkg^{-1} respectively, while concentrations of Cu were 45.43 mgkg^{-1} in K-C1 and 48.88 mgkg^{-1} in K-S1. Concentrations of Pb and Cd in all samples are low.

Table 4. **Concentration of heavy metals**

Heavy metal (mgkg-^{1})	K-C1	K-S1	R-C1	R-S1
Ni	3364.00 ±41.14	1050.00 ± 34.46	1525.00 ±92.20	2209.00 ±71.36
Cr	1126.00 ±16.36	2568.00 ±23.61	291.00 ±23.82	2221.00 ±19.49
Zn	81.25 ±8.84	55.00 ±10.21	159.17 ±23.06	132.50 ±62.34
Cu	45.43 ±18.22	48.88 ±4.07	54.11 ±9.23	49.75 ±21.55
Pb	32.80 ±12.54	40.58 ±2.00	10.28 ±2.61	6.40 ±2.91
Cd	0.79 ±0.23	1.01 ±0.15	0.81 ±0.38	1.10 ±0.55

CONCLUSION

Soil and concretion samples from Ranau and Kundasang have been successfully characterized in terms of magnetic properties, mineralogy and heavy metals content. Magnetization measurement have shown that samples K-S1, R-S1 and R-C1 fall within in pseudo-single domain (PSD) grains, while K-C1 falls in multi domain (MD) grains. The XRD measurement have confirmed that the magnetic characteristics in soils are due to the presence of magnetic minerals called hematite (α-Fe$_2$O$_3$). The concentration of heavy metals demonstrated high content of Ni and Cr. Concentration of other elements (Zn, Cu, Pb and Cd) were found less than 55 mgkg^{-1}.

ACKNOWLEDGEMENTS

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