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GEOCHEMICAL ASSESSMENT OF METAL TRANSFER FROM ROCK AND SOIL TO WATER IN SERPENTINE AREAS OF SABAH (MALAYSIA)

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ABSTRACT

The mobility of metals in ultramafic rock–soil systems and metal contamination in serpentine soils were investigated from the Ranau area in Sabah, East Malaysia. Metal concentrations were analysed after division into seven operationally defined fractions by selective sequen-tial extraction (SSE). Geochemical studies showed that the soils are exceptionally high in Cr (\19,000 mg kg-1), Ni (\4800 mg kg-1) and Co (\170 mg kg-1), about 140, 16 and 10 times higher than global soil averages, respectively. Thus, the soil can be categorized as unusually contami-nated in comparison with relevant guidelines. Neverthe-less, despite expectations, low concentrations of Cr, Ni and Co were found in surface waters flowing over the serpen-tine massifs (\14, 94 and 7 lg L-1, respectively), indi-cating mobile ingress into river waters is low or, alternatively, diluted in the tropical environment resulting in minimal decline in their quality ascribed to the regional ultramafic geology of the area. The main reason is revealed by the SSE finding of very low (\1%) mobile metal abundances in available fractions of Ranau soils. While this study is one of the first to use a comprehensive SSE in tropical serpentine soils, the major SSE finding highlights the majority of metals ([95%) residing in refractory residual fractions. Metal speciation studies will shed further light on toxicities in the Malaysian ultramafic tropical environment, reconciled against elemental metal tenure, adopted by common standards.

Keywords: Serpentinite, lateritic soil, surface water, heavy metal, mobility

1. Introduction

Serpentinites are hydrothermally altered ultramafic rocks with heavy metal enrichment compared to many other rock types, which cover about 1% of the earth's surface (Tur-ekian and Wedepohl 1961; Brooks 1987; Proctor 2003). It is well documented that a substantial quantity of side-rophile elements including chromium (Cr), nickel (Ni) and cobalt (Co) in these rocks are exceptionally high compared to the Earth's crust. The concentrations, fractionation and availability of metals in soils over ultramafic rocks throughout the world have been extensively studied (Tur-ekian and Wedepohl 1961; Schwertmann and Latham 1986; Graham et al. 1990; Bonifacio et al. 1997; Dinelli et al. 1997; Shallari et al. 1998; Godard et al. 2000; Quantin et al. 2002b; Proctor 2003; Lee et al. 2004; Brearley 2005; Skordas and Kelepertsis 2005; Becquer et al. 2006; Kierczak et al. 2007; Rashmi et al. 2009; Alves et al. 2011; Tashakor et al. 2014a). The concentrations up to 125,000 mg kg-1 Cr (Adriano 2001) and more than 10,000 mg kg-1 Ni (Hseu 2006) were observed in ser-pentinite soils, while the concentration of these metals in other soils commonly ranges up to 100 mg kg-1 (Kabata-Pendias 2000). Heavy metals in the environment are receiving increasing attention among soil scientists and biologists (Ashraf et al. 2015) due to growing scientific and public awareness of their polluting and potential carcinogenic role, with heavy metal contamination representing a significant challenge due to their persistence in the environment. While metals from anthropogenic origins are often considered to be more of an environmental problem, lithogenic metal release should be considered in certain areas, such as those over ultramafic rocks. Soils over ultramafic rocks represent sources of natural geogenic contamination (Oze et al. 2004; Hseu et al. 2007; Kierczak et al. 2008), particularly in areas where there are significant human populations. It is not surprising that parent rock metal content is transferred to soils, though their geo-chemical and mineralogical characteristics have the potential to alter metal tenure and mobility, and therefore influence the environment with possible knock-on effects on human health. These soil quality issues are particularly important in South-East Asia given the presence of large area of ultramafic rocks (Repin 1998; Proctor 2003; Tashakor et al. 2014b; van der Ent et al. 2016). The natural metal sources can be traced back to geological and pedo-genic processes through which metals are liberated from parent materials and may enter the wider environment. However, it is more important to understand the stocks and fluxes within and between different fractions in which such metals are held in rocks and soils if we are to gain a full understanding of the importance of ultramafic lithologies in potential geogenic contamination. Though emphasis is often placed on the role of pH in mobility and solubility of metals, the presence of soil organic matter, oxides and hydroxides plays an inhibiting role in release of metallic elements. In fact, our findings and others (Kaasalainen and Yli-Halla 2003) show the affinity of heavy metals to bind with different soil fractions, which may vary significantly, determines how strongly metals are retained in soils and how easily they might be released into soil solution and subsequently to adjacent surface waters (Vardaki and Kelepertsis 1999; Cance`s et al. 2003). As soil is composed of a heterogeneous mixture of organic and inorganic con-stituents with varying ability to interact physically and chemically with heavy metals, metals present in soils can be associated with several reactive components. Soil metal mobility is limited largely by initial mineralogical specia-tion and subsequent metal binding forms associated with soil constituents and/or speciation that may partition into various soil fractions. Based on the affinity of metals to bind with different soil constituents, they are defined rep-resenting a decreasing degree of metal availability, ranging from ions in soil solution to ions in rock crystal lattices that can be assessed using sequential extraction procedures (Tessier et al. 1979; Silveira et al. 2006). Few studies have addressed potential pollutants in water resources and agricultural or natural soils resulting from the large regio-nal extent of ultramafic rocks in the Malaysian tropical setting, particularly with methods revealing species contributions such as the selective sequential extraction (SSE) method. This is one of the first studies using a combination of mineralogical analysis (XRD), elemental content (XRF) and soil physical and chemical character-istics, in which we aim to determine the availability of metals in rocks, soils and waters in such environments. It therefore contributes to our understanding of potential health effects on populations living on or near ultramafic lithologies.

2. Materials and methods

2.1. Study area and sampling

Sabah is one of the two Malaysian states located in north-west Borneo. Ultramafic peridotite outcrops extend widely over about 3500 km2 (Repin 1998). The current study focuses on the Ranau area in north-west Sabah between the latitudes of 5L570 –6L020 N and longitudes of 116L400 – 116L450 E (Fig. 1) where the ultramafic series forms a broad expanse of land covering about 41 km2 (Hing 1969). The common rock types in the area are tremolite peridotites and spinel lherzolites (Hutchison 2005). However, peridotites of Ranau are partially to totally altered through intense serpentinization and weathering and are difficult to recog-nize in the field. Serpentinites are characterized by their blue colour with small ill-defined greenish lenses. Their appearance is waxy, although some specimens appear to be crystalline. Associated metamorphic rocks are greenschists and amphibolites. The serpentinites are in fault contacts associated with hornblende gabbro. Diabase dikes intrude the ultramafic formations in some areas. The sedimentary rocks of the Ranau area are mainly associated with the north-west Borneo eugeosyncline of late Cretaceous to Tertiary age. These sedimentary rocks (Trusmadi or Crocker formations) consist of thick successions of sand-stones and shale.

Four rock and ten soil samples (\20 cm depth including A and upper B horizons) were taken from the environs of the villages of Kinaratuan, Lohan Skim 1 and 2, Lohan Ulu and Tuhan (Fig. 1). Soils were taken from upper horizons after removal of debris and vegetation. Water sampling (from c. 10 cm depth) included samples taken from rivers flowing over serpentinites, namely Bongkud, Liwagu, Lohan, Napatau and Takorek. The focus of this study is on the surface water composition, though additional seepage water from Lohan Ulu, col-lected by hand pumping through a plastic pipe, was also analysed for comparison. Samples of 150 mL were kept in pre-washed polyethylene containers, and 2 mL of con-centrated high-purity HNO3 was added to each of them to preserve the samples and avoid precipitation of oxyanions. They were analysed elementally by ICP-MS (Perkin-Elmer ELAN 9000).

2.2 Soil physical and chemical characterization

Particle size distribution of soil samples was determined using the hydrometer method (British Standard Institution 1990). The pH was measured in a 1:2.5 (w:v) soil:distilled water suspension. The cation exchange capacity (CEC) was calculated by summation of Ca, Mg, K, Na and titrat-able acidity, all extracted with 1 M ammonium acetate (CH3COONH4). The solutions were filtered through cel-lulose nitrate membrane filters (45 lm) and were analysed elementally by ICP-MS (as above).

2.3 Mineralogical analyses

X-ray diffraction (XRD) analysis of ten air-dried, pulverised and sieved (< 2 mm) soil samples was performed on a Bruker D8 Advance diffractometer. The analysing radiation was Cu*K*α with a wavelength of 1.5406 Å (0.15406 nm). X-ray diffractograms were collected on powder samples within the 2h range [5L–60L], with 0.02L 0.1 s step.

2.4 Bulk elemental analyses

The bulk chemical composition of rock and soil samples was determined by X-ray fluorescence spectrometry (XRF) using a Bruker S8 Tiger X-ray with the exciting energy source of Rhodium K-α line. In order to measure 10 major oxides (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5**)**, the powdered soils (< 30 μm) were made into 32 mm diameter fused-beads, by igniting 0.5 g of sample with 5.0 g of Johnson-Matthey Spectroflux 110, giving a dilution ratio of 1:10 by igniting. To measure trace elements (Appendix A1), pressed-powder pellets were prepared by applying a pressure of 20 tonnes for one minute to 1 g of sample with 6 g of pure boric acid powder.

2.5 Elemental speciation

Chromium, Ni and Co were fractionated with the seven-step extraction procedure scheme proposed by Tessier et al. (1979) and modified by Silveira et al. (2006) (Table 1). This method is adapted for tropical Oxisols in which the mineralogy is dominated by Fe and Mn oxides and pro-vides data on operationally defined soil fractions. Unlike many extraction procedures, the extraction scheme of Sil-veira et al. (2006) is capable of differentiating metals trapped in amorphous or poorly crystalline oxides from crystalline forms. Selective sequential extraction was performed using 1 g of air-dried and sieved soil samples (\2 mm) in 50-mL polycarbonate centrifuge tubes. Reagents were added in a stepwise fashion to digest the soils, and the suspensions were equilibrated as described in Table 1. The supernatants were separated from the solid phases by centrifugation for 18–24 h at 12,880 RCF. They were then filtered through 45-lm cellulose nitrate mem-brane filters and analysed by ICP-MS (as above) following each stage of extraction.

2.6 Data quality

All samples were analysed in duplicate to verify the pre-cision of analysis; the relative percentage difference between duplicate measurements was always less than 10%. Precision of the ICP-MS was shown by analysing the international reference standard STD 125 ppb-1 five times giving a relative standard deviation of less than 1.6% in all cases. Detection limits for Cr, Ni and Co were 0.05 lg g-1 and 0.1 lg L-1 for soil and water samples, respectively. The international standard for corundum was used as a reference material for the XRD analysis, whereas several certified reference materials with varying SiO2 content (USGS-BCR-2, SO-2, W-2a, CANMET SY-2 and CRPG-GSN) were analysed by XRF. There are no reference materials certified for all steps of the SSE, so, in order to evaluate the extraction efficiency, the concentrations of the various forms of Cr, Ni and Co were summed after extraction from each sample and compared to their total concentration obtained by XRF determination of the bulk sample.

3. Results and discussion

3.1 Mineralogical composition of rocks and soils

The rock mineral assemblage is characteristic for ultramafics containing antigorite, chrysotile and lizardite (Figure 2). Different types of spinel, especially chromite and magnetite also occur in the rocks. The studied serpentinite-derived soils typically showed representative feature of tropical soils with major contents of oxides and hydrous oxides dominated by hematite and including goethite (that are weathering products of magnetite) (Figure 2). The serpentine soils typically contain chromite and minor amounts of chlorite and ilmenite and trace amounts of inherited serpentine minerals are also recognized. The dominant clay mineral is kaolinite. Allochthonous quartz is present in almost all the analysed soil samples, probably related to their eolian origin.

3.2 Bulk composition of serpentinite rocks and soils

The mean SiO_2 content in the rocks was 43.2 % (by weight) (Table 3). The mean content of MgO was 35.5 % and Fe_2O_3 showed a mean content of 8.8 % (Table 3). The mean CaO content was very low (2.5 %) as were Na_2O (0.18 %), K_2O (0.09 %) and P_2O_5 (0.01 %). Analyses of major oxides of rocks from Ranau accords with the chemical compositions of numerous ultramafic massifs throughout the world listed by Brooks (1987). Among the twenty trace metals analysed, Cr, Ni and Co are considered further (Table 3). The total concentrations of Cr and Ni range from 2622 to 2781mg kg^{-1} and 1602 to 1840 mg kg^{-1}, respectively and the observed range of Co was between 61 and 64 mg kg^{-1}. The former two elements are notably higher compared to the average Earth's crust (Cr: 100 mg kg^{-1} and Ni: 25 mg kg^{-1}) (Mason and Moore 1982). The most striking result with regard to the soils was, again, notably high concentrations of Cr, Ni and Co (Table 3). Chromium in Ranau soils had a high mean value of 14,208 mg kg^{-1} (range: 2,427 to 27,863 mg kg^{-1}). The World Cr concentrations in soils range up to 200 mg kg^{-1} (Bourrelier & Berthelin 1998); however, in the presence of ultramafic bedrocks, such as serpentinites, the Cr concentration is up to 10,000 mg kg^{-1} (Stueber and Goles 1967; Schwertmann and Latham 1986). This study showed a mean Ni concentration of 1,647 mg kg^{-1} (range: 850 to 4753 mg kg^{-1}). The common background average for Ni is less than 100 mg kg^{-1} (Kabata-Pendias 2000) while numerous studies have reported Ni concentrations of more than 10,000 mg kg^{-1} in ultramafic soils (Brooks 1987; Hseu 2006). Cobalt had a mean of 112 mg kg^{-1} and ranged from 35 to 167 mg kg^{-1}. According to Kabata-Pendias and Mukherjee (2007), surface soil Co ranges from 4.5 to 12 mg kg^{-1}. Chromium, Ni and Co concentrations in serpentinite rocks and soils of Sabah were also in agreement with the reported values from serpentinites of India (Rashmi et al. 2009), Oman (Godard et al. 2000), Greece (Skordas and Kelepertsis 2005), and Iran (Ghaderian and Baker 2007). Nevertheless, serpentinite soils of New Caledonia contained much higher concentrations of Cr (31,000 mg kg^{-1}) and Ni (12,000 mg kg^{-1}) (Massoura et al. 2006). SiO_2 shows strong positive correlation with CaO (0.81), Na_2O (0.82) and K_2O (0.87) (Appendix) and these alkali and alkali earth elements also indicate the same correlation with each other, whereas Fe_2O_3 forms another very strongly correlated pair with MnO having a correla-tion coefficient of 0.80. Cobalt and Cr correlate with this group showing strong coefficients: Fe_2O_3–Co (0.66), Fe_2O_3–Cr (0.80), MnO–Co (0.61) and MnO–Cr (0.67). There is a strong positive correlation between Cr and Co (0.96). However, Ni presents a different behaviour and shows moderate association with MgO with a correlation coefficient of 0.60 due to its calchophile nature.

3.3 Physico-chemical characteristics of soils

The soils are slightly acidic, showing a mean pH value of 5.8 ± 0.6 (Table 2). The pH ranges from 5.2 to 7.2 in line with soils derived from mafic and ultramafic rocks in lowland tropical regions (Brearley 2005; Massoura et al. 2006; Garnier et al. 2009). Silt is the predominant fraction in all of the soils except for sample S12, which is mainly composed of clay particles (Table 2). The soils are thus classified as silty loam to silty clay loam and clay (Soil Survey Division Staff 1993). Cation exchange capacity (CEC) shows a broad range with a mean of 12.0 ± 10.4 cmol(+) kg^{-1} (Table 2); the CEC was dominated by exchangeable Mg^{2+} with the mean value of 11.3 ± 10.2 cmol(+) kg^{-1}, over 90 % of the mean CEC. The highest CEC was shown by sample S3 (33.9 cmol(+) kg^{-1}), followed by clay sample S12 (23.7 cmol(+) kg^{-1}). Sample S4 showed the lowest CEC (1.2 cmol(+) kg^{-1}), near a regional contact inflexion, and possible faulting, approximately midway between the highest S3 and S12 CEC samples.

3.4 Enrichment and depletion of elements from rocks to soils

During chemical weathering and pedogeological processes, the concentrations of certain elements from the parent rocks may significantly increase or decrease in the resultant soils (Osama 2007). Al_2O_3 and MnO were minor components of bulk rock composition, while the amounts of these elements showed a three to five-fold increase in derived soils along with Fe_2O_3 (Table 3). The concentrations of Cr and Co were also enriched five and two times, respectively in the soils compared to parent materials. The concentration of Ni in the soils was equal to that in the parent rocks whereas MgO showed a ten-fold depletion. The observed enrichment and depletion pattern in this study is similar to that proposed by Kostić et al. (1998) for wet environments. In general, tropical climates, by inducing intense and complete hydrolysis, lead to the immobilization of poorly leachable metals in the secondary minerals and oxides and accumulation in soil profiles, especially toward the surface. During the pedogenesis of serpentinite, highly mobile elements such as Mg and Si leach from the soil profile at the early stages of weathering, while newly formed clay minerals become enriched in less mobile elements such as Fe and Al.

3.5 Distribution of Cr, Ni and Co in various soil fractions

The difference between the total metal concentrations (by XRF) and the sum of the concentration of metals extracted from each step of the SSE analysis, was less than 20% in all cases indicating a reliable extraction (Tessier et al. 1979). The SSE indicated the main incorporation of Cr and Ni was within the residual fractions of soils (Figure 3); this was 12256 mg kg^{-1} for Cr and 1233 mg kg^{-1} representing 92.3% and 89.8% of the total extracted metals (assuming the XRF analyses represent the total concentration of the metals). Combining this result with mineralogical observation, we conclude Cr and Ni are bound in serpentine minerals and chromite spinels that are highly resistant to weathering, extracted only at the last stage using strong acidic reagents. This is in agreement with other research in New Caledonia (Quantin et al. 2002a), Brazil (Garnier et al. 2009), Poland (Kierczak et al. 2008) and Taiwan (Cheng et al. 2011). The use of microscopic (e.g. synchrotron, EDX, electron microprobe) techniques would aid further research to determine the co-location of these metals with certain primary or secondary minerals. Amorphous (poorly-crystalline) and crystalline Fe-oxide and Mn-oxide fractions were the most abundant metal pools among the non-residual fractions, as predicted for 'lateritic' tropical soils. About 3.3% of the total extracted Cr (432 mg kg^{-1}) was 'trapped' in the crystalline Fe-oxide fraction and the concentration of Cr in the Mn-oxide fraction (371 mg kg^{-1}; 2.8%) was higher than that in the poorly-crystalline Fe-oxide fraction (135 mg kg^{-1}; 1.0 %). With respect to Ni, a preferential association with crystalline Fe-oxide (73 mg kg^{-1}; 5.0%) rather than with poorly-crystalline Fe-oxide (25 mg kg^{-1}; 1.6%) or Mn-oxide (mg kg^{-1}; 3.3%) was observed. This result is in agreement with the work of Garnier et al. (2009) who found Ni to be preferentially associated with crystalline Fe-oxide over poorly-crystalline Fe-oxide and Alves et al. (2011) who found comparable amounts of Ni in crystalline Fe-oxides compared with poorly-crystalline Fe-oxide plus Mn-oxides. However, it contrasts with the work of Massoura et al. (2006) who suggested that in highly weathered tropical soils, a higher proportion of the Ni should be found in the poorly-crystalline Fe-oxide fraction. Van der Ent et al. (2016) found higher Ni in the amorphous Fe-oxides (< 30 %) and crystalline F-oxides (< 10 %). However thses soils were under Ni-hyperaccumulator plants with > 0.01 % Ni in plant parts that may recycle and concentrate Ni in uper soils prefering to grow in highly weatheed deep soil. In comparison to Cr and Ni, Co revealed a much higher affinity for the Mn-oxide fraction of soils (65.6 mg g^{-1}; 58%) in addition to its abundance in the residual fraction (mean = 24.8 mg g^{-1}; 23%). The non-resistant components including the first three fractions of soluble-exchangeable, surface adsorbed and organic matter contained very small quantities (less than 1.5 % in total) of Cr, Ni and Co of the total soil extracted in all the samples. This suggests that the metals of concern are not easily leachable and thus not readily transferable within the environment under ambient conditions. This is also influenced by the nature of these soils being low in organic matter as soils with greater organic matter content are likely to have more Ni in organic fractions (Hseu et al. 2016).

3.6 The 'quality' of serpentinite soils

The mean concentrations of Cr, Ni and Co in the serpentine soils are about 130, 40 and 10 times higher than average global soil composition (Table 4). Using the geoaccumulation index (I*geo*) of Müller (1969) and the background values for relevant soil Fe concentrations from Hamon et al. (2004), we determined that the soils were moderately to strongly contaminated (I*geo* class 3 on a six-point scale) by Ni and strongly contaminated (I*geo* class 4) by Cr. Based on the concentration of Cr and Ni, all the soils were attributed to group C in the Dutchlist (2009) standard (indicating significant pollution and a serious toxic threat to the environment), while the Co concentration corresponds to group B (referring to soils with pollution that may lead to possible harmful effects (Table 4). Comparing with soil quality guidelines developed by Australian and New Zealand Environment and Conservation Council (ANZECC/NHMRC 1992), the concentration of Cr in the studied soils is about two orders of magnitude higher than the maximum background value for Cr (110 mg kg^{-1}). Similarly, Ni in the investigated soils exceeds the higher background concentration level (400 mg kg^{-1}) given by ANZECC/NHMRC (1992). Thus, the metals in the surveyed serpentinite soils are also considered pollutants on this standard. Using the Greater London Council (2001) guidelines: with regard to Ni and Cr, the soils are categorised as ‘unusually heavily contaminated’, which is point 5 on a five-point scale; these guidelines do not furnish any classification for Co contamination. It should, of course, be noted that these standards don't necessarily relate to the specifics of tropical soil characteristics as they were largely and obscurely adopted from European standards (McLaughlin et al. 2000). In a comprehensive study, Zarcinas et al. (2004), suggested the 95th percentile values of the randomly 241 selected soils sampled from Peninsular Malaysia as “Investigation Level” (Table 4); this would apply to all soils sampled from Ranau in this study. Nevertheless, the 95th percentile via random sampling does not reconcile differing parent geology, mineralogy and climate or the interactions between them to either mitigate or accelerate potential bio-toxicity.

3.7 Metal concentrations in waters

Surprisingly, few studies have examined metal concentrations in water samples over ultramafic areas; those found here were comparable to those observed by Vardaki & Kelepertsis (1999) in Greece and Migon et al. (2011) in New Caledonia although Cr was, in general, lower. The maximum concentrations of Cr (14 µg l^{-1}), Ni (94 µg l^{-1}) and Co (7 µg l^{-1}) in river samples (Table 5) were lower than the maximum permissible values (Cr: 50 µg l^{-1}, Ni: 200 µg l^{-1}, Co: 50 µg l^{-1}) proposed by Interim National Water Quality Standards of Malaysia (INWQS 2006). The metal concentrations in Ranau rivers also compared reasonably, with the World Health Organization (WHO 2006) standard of 50 µg l^{-1} Cr and 70 µg l^{-1} Ni and the United States drinking water quality guideline (EPA 2009) of 100 µg l^{-1} Cr . It was found that Cr, Ni and Co in all of the rivers flowing over serpentine soils fell within these 'permitted' INWQS thresholds and the majority, with exception of peak Ni, were within the WHO threshold. Hence, according to these published standards, these rivers, limited by sampling constraints presented, appear safe both for drinking water and crop production. It must be noted, however, this does not address ionic complexion, speciation factors, for Cr in particular, and the potential bio-toxicity thereof. The seepage water sample analysed, however, had a Ni concentration considerably higher than in surface waters (Table 5) and clearly in excess of standards for Ni. It is conceivable that more extensive seep water sampling and more local fluvial waters will reveal analyses in excess of threshold standards. Possible reasons include low volume of seepage water relative to larger rivers subject to high flow surface run-off, regional outlier geological provenance dilution and local to regional metal precipitation through oxyanion species. Whilst sampling was limited, evidently local seepage waters that ingress and flow through serpentine soil profiles do become enriched in these elements. Lottermoser (1997) believed almost all seepage and groundwater associated with ultramafic formations have elements beyond environmental quality guidelines in accordance with findings of this study showing, concentration of Ni up to 9 times higher than INWQS standards, though Cr and Co in the seepage water are still within the 'safe' limits, albeit with the potential caveats aforementioned.

3.8 The relationship between Cr, Ni and Co in soil and surface water

This study showed that the geochemistry of the ultramafic parent materials has a minor effect on the chemical composition of regional flowing surface waters. This may be due to various factors, as noted above, though, this study reveals the low contribution of the metals in the easily leachable and exchangeable fractions of soils is the main factor responsible. The metals concerned are held mainly in the residual fraction of soils as refractory latticed minerals and secondly sorbed in the oxide and hydroxides of Fe and Mn with relatively high affinity as liganded species. Therefore, in accordance with previous studies (Becquer et al. 2003; Massoura et al. 2006), Cr, Ni and Co in the studied soils have low mobility with little tendency to readily migrate into the environment. On the other hand, the solubility of Cr and Ni in surface water is pH dependent to some degree. Chromium is soluble at pH values of less than 4 and the solubility of Ni occurs only at pH value of less than 5.5 (Rahim et al. 1996). The pH values of the investigated soils ranged from slightly acidic to circumneutral preventing significant metal solubility. In addition, the soils displayed a fine granular structure and a silty loam to silty clay loam texture. Since silt and clay grain size fractions, by having a larger specific surface area, are capable of adsorbing more metals, it is assumed that these soils bound higher concentrations of metals and low propensity to release them into the environment. In addition, the aerobic status of soils may affect metal release as waterlogged conditions may lead to the release of metals by reductive dissolution of Fe- and Mn-oxides (Rinklebe et al. 2016).

4. Conclusions and prospects

Malaysian serpentinites studied here showed a ferromagnesian mineralogy with high concentrations of Cr, Ni and Co suggesting they are capable of inducing serious natural pollution. However, surface waters flowing over serpentinite soils revealed minimal notable concentration of Cr, Ni and Co, and are considered ‘safe’ as defined by relevant threshold standards. Consequently, for the most part, chemical composition of surface water is concluded to ineffectively reflect bedrock and soil geochemistry of regional expanses of serpentinites. The main reason for this is concluded to be the very low proportion of metals associated with the easily leachable and ion exchangeable fractions of the soils. Being largely immobile, ingress of these metals into surface waters via leaching is minimized and subsequent dilution may be expected to further minimize wider fluvial metal transport and contamination. Therefore, despite their anomalously high natural concentrations of certain metals, these serpentine soils are not considered to pose a health or environmental risk. However, further work should examine metal speciation and soil Cr is of particular interest, given Cr^{3+} is considered an essential nutrient and Cr^{6+} carcinogenic.

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Table 1. Sequential extraction procedure for metals in tropical soils as proposed by Silveira et al. (2006)

Fraction	**Solution**	**Equilibrium conditions**
Soluble-exchangeable	15 ml 0.1M $CaCl_2.2H_2O$	2 h, room temperature
Surface adsorbed	30 ml 1 M NaOAC (at pH 5 with CH_3CO_2H)	5 h, room temperature
Organic matter	5 ml NaOCl (at pH 8.5 with HCl)	30 min, 90–95 °C
Mn-oxides	30 ml 0.05 M $NH_2OH.HCl$ (at pH 2 with HCl)	30 min, room temperature
Poor crystalline Fe-oxides	30 ml 0.2 M $H_2C_2O_2$ + 0.2 M $(NH_4)_2C_2O_4$ (at pH 3 with NH_4OH)	2 h, dark
Crystalline Fe-oxides	40 ml 6 M HCl	24 h, room temperature
Residual	HNO_3–HCl.HF + 1.5 % H_3BO_3 digestion	3050b

Source: Silveira et al. (2006)

Table 2. Physical and chemical characteristics of serpentine soils from Ranau, Sabah (Malaysian Borneo)

		S1	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S10**	**S12**	**S13**	**Mean ± SD**
pH		5.6	7.2	5.8	5.7	5.4	5.8	5.2	5.3	5.9	6.4	5.8 ± 0.6
> 2 mm (%)		1	0	0	0	0	0	1	2	0	1	0.5 ± 0.7
< 2 mm	Sand (%)	25	20	33	19	30	30	22	18	20	19	23.6 ± 5.5
	Silt (%)	58	52	54	50	52	55	59	48	25	51	50.4 ± 9.6
	Clay (%)	16	28	13	31	18	15	18	32	55	29	25.5± 12.6
Texture		Silt loam	Silt clay loam	Silt loam	Silt clay loam	Silt loam	Silt loam	Silt loam	Silt clay loam	Clay	Silt clay loam	
Exchangeable cations (cmol(+) kg^{-1})												
CEC		5.3	33.9	1.2	11.8	7.3	3.7	3.2	12.0	23.7	17.8	12.0 ± 10.4
Mg^{2+}		4.9	33.5	0.9	11.2	7.0	3.5	2.4	11.0	21.4	17.4	11.3 ± 10.2
Ca^{2+}		0.3	0.3	0.1	0.6	0.2	0.1	0.4	0.3	0.4	0.2	0.3 ± 0.1
K^{+}		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.2	0.0	0.0 ± 0.1
Na^{+}		0.2	0.1	0.1	0.1	0.1	0.1	0.4	0.5	1.7	0.2	0.4 ± 0.5

Table 3. The concentration of major oxides and trace elements in serpentinite rocks and soils of Ranau, Sabah (Malaysian Borneo), Enrichment or depletion factors are the ratio between the concentration of the element of interest in the rock compared to the soil; significant differences ($p < 0.05$) are marked by an asterisk

		Major oxides (wt%)										Trace metals (µg/g)		
		SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Co	Cr	Ni
Rock	**R.1**	43.20	0.14	3.23	8.74	0.12	35.45	2.75	0.23	0.09	0.01	63	2743	1609
	R.3	42.60	0.08	2.29	8.53	0.12	37.32	1.80	0.10	0.09	0.00	64	2622	1840
	R.4	43.70	0.17	3.71	9.17	0.13	35.32	3.20	0.23	0.09	0.01	62	2641	1602
	R.7	42.50	0.14	3.41	8.92	0.11	34.07	2.40	0.14	0.10	0.00	61	2781	1658
	Mean ± SD	43.20 ± 0.50	0.13 ± 0.03	3.20 ± 0.60	8.84 ± 0.30	0.12 ± 0.01	35.54 ± 1.34	2.54 ± 0.59	0.18 ± 0.07	0.09 ± 0.01	0.01 ± 0.01	62 ± 1	2697 ± 77	1677 ± 111
Soil	**S1**	60.50	0.63	16.84	11.35	0.08	0.76	0.36	0.09	1.95	0.12	136	13929	1675
	S3	26.40	0.25	9.77	41.04	0.73	8.47	0.10	0.05	0.00	0.05	122	14720	2237
	S4	14.50	0.47	17.75	38.82	0.59	2.83	0.03	0.01	0.00	0.03	146	16381	1573
	S5	5.10	0.94	22.89	42.69	0.29	0.31	0.04	0.03	0.00	0.05	112	14029	850
	S6	17.60	0.24	12.85	42.90	0.75	7.97	0.17	0.07	0.00	0.04	167	19025	4753
	S7	13.60	0.61	19.34	45.47	0.81	0.86	0.02	0.02	0.00	0.04	127	17233	1219
	S8	58.00	0.61	10.18	11.47	0.17	3.70	0.13	0.16	0.63	0.02	35	2427	865
	S10	19.10	0.99	22.63	42.05	0.40	1.31	0.09	0.04	0.01	0.06	114	15807	1311
	S12	25.30	0.29	5.87	25.62	0.12	0.29	0.10	0.00	0.01	0.04	93	11277	972
	S13	54.60	0.57	11.88	12.78	0.18	8.71	0.33	0.11	1.26	0.02	46	2828	1418
	Mean ± SD	29.47 ± 20.42	0.56 ± 0.26	15.00 ± 5.76	31.42 ± 14.52	0.41 ± 0.28	3.52 ± 3.52	0.10 ± 0.11	0.06 ± 0.05	0.40 ± 0.70	0.04 ± 0.02	109 ± 41	12766 ± 5736	1687 ± 1156
Enrichment & depletion factors		0.68	4.3 *	4.69*	3.55*	3.42*	0.10*	0.04*	0.33*	4.32	8.00*	1.76*	4.73*	1.01

Table 4. The mean concentration of chromium, nickel and cobalt in serpentine soil samples from Ranau, Sabah (Malaysian Borneo) and their geoaccumulation index enrichment (I*geo*) in comparison with the average Earth composition, the 95% 'Investigation Levels' determined for Malaysia, ANZECC/NHMRC and Greater London Council guideline (all values are mg kg^{-1})

	Ranau soil	**I*geo*[1]**	**Average Earth soil composition[2]**	**Malaysian Investigation Levels[3]**	**ANZECC/NHMRC[4]**		**Greater London Council guidelines[5]**				
					Background level	Environmental investigation	I	II	III	IV	V
Cr	12,766	3.29	100	60	0.5-110	50	100	200	500	2500	>2500
Ni	1687	2.39	40	45	2-400	60	20	50	200	1000	>1000
Co	109	-	10	10	2-170	-	-	-	-	-	-

[1] I*geo* = log2 (M/ 1.5 x B_n) where M is the concentration of metal in soil and B_n is the background concentration of metal (Müller 1969).

[2] Average soil composition from Siegel (1975).

[3] The 95% 'Investigation Levels' determined for Peninsular Malaysia (n=241 soils) (Zarcinas et al. 2004).

[4] Soil quality guideline developed by Australian and New Zealand Environment and Conservation Council (ANZECC/NHMRC 1992).

[5] Greater London Council guidelines (G.L.C (2001) definitions of contaminated soils (I = Typical values for uncontaminated soils, II = Slight contamination, III = Contaminated, IV = Heavy contamination, V = Unusually heavy contamination)

Table 5. Concentrations of chromium, nickel and cobalt in river and seeping water traversing serpentinites of Ranau, Sabah (Malaysian Borneo)

	Sample ID	**Cr** ($\mu g\ l^{-1}$)	**Ni** ($\mu g\ l^{-1}$)	**Co** ($\mu g\ l^{-1}$)
Surface water	W3	14	42	2
	W5	7	23	1
	W8	5	67	1
	W9	8	18	2
	W12	6	11	2
	W13	9	42	5
	W14	7	20	4
	W20	11	94	7
	Mean ± SD	8.3 ± 2.7	39.7 ± 26.6	3.0 ± 2.0
Seeping water	W4	23	936	22
Threshold Standards	WHO[1]	50	70	-
	INWQS[2]	50	200	50
	EPA[3]	100	-	-

[1] World Health Organization (WHO 2006)

[2] Interim National Water Quality Standards for Malaysia (INWQS 2006)

[3] United States drinking water quality guideline (EPA 2009)

Fig 1. Map of Ranau area (Sabah, Malaysian Borneo) studying on the geochemistry of metal transfer between rocks, soils and water. Sampling locations are noted as rock (R), soil (S) and water (W)

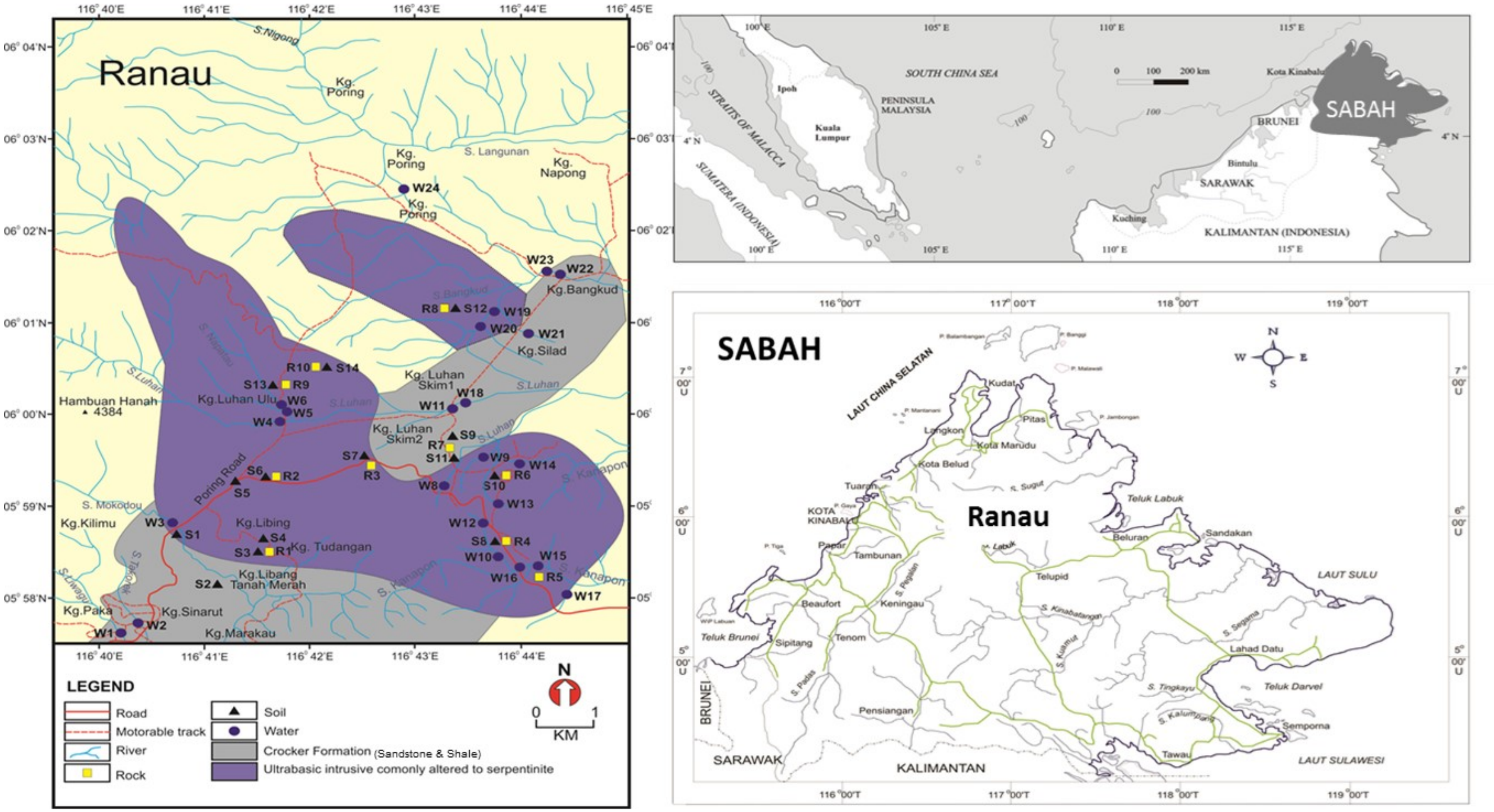


Fig 2. X-ray diffractograms of representative serpentinite rock (left) and soil (right) samples in the vicinity of Ranau, Sabah (Malaysian Borneo)

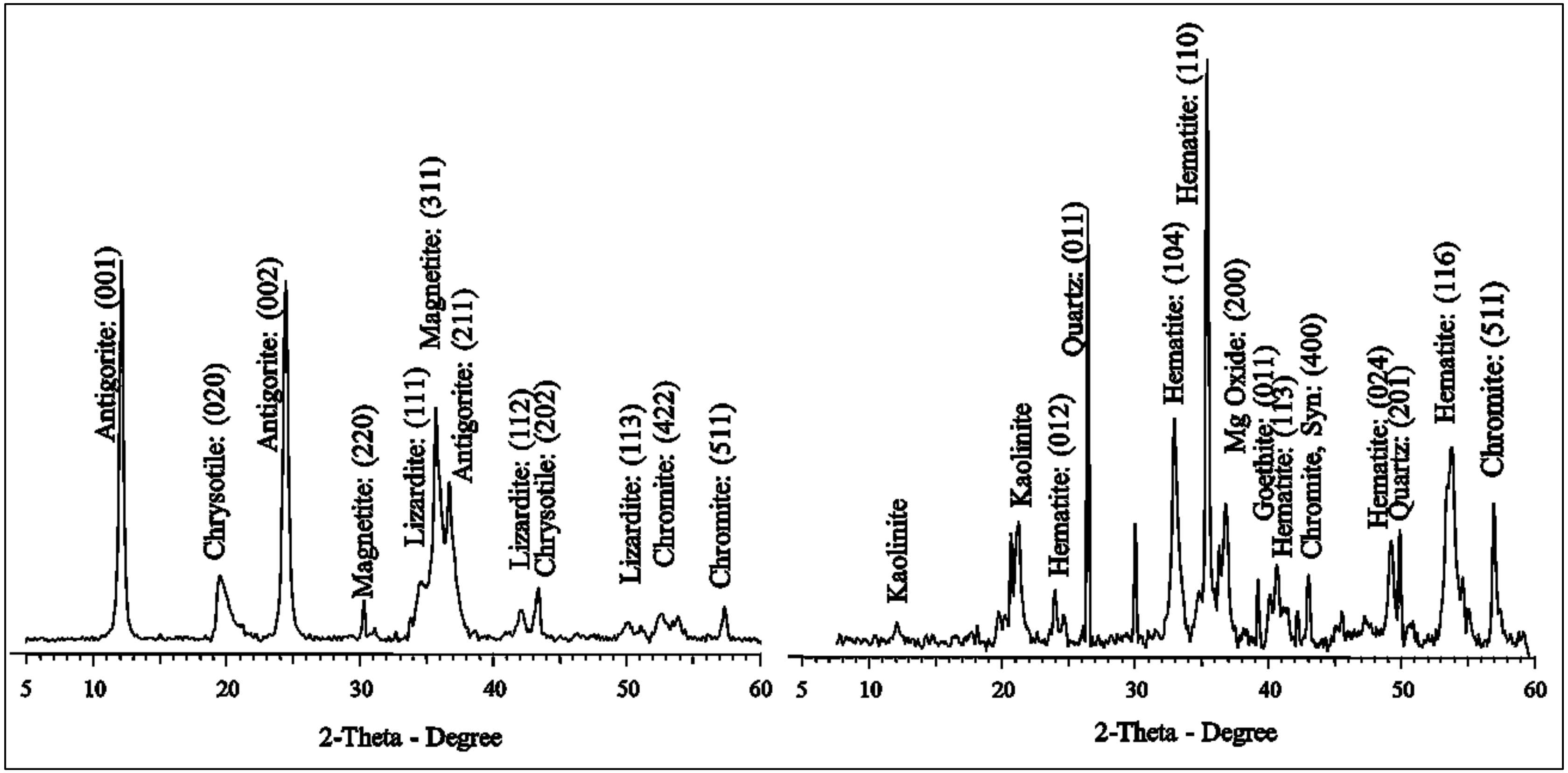
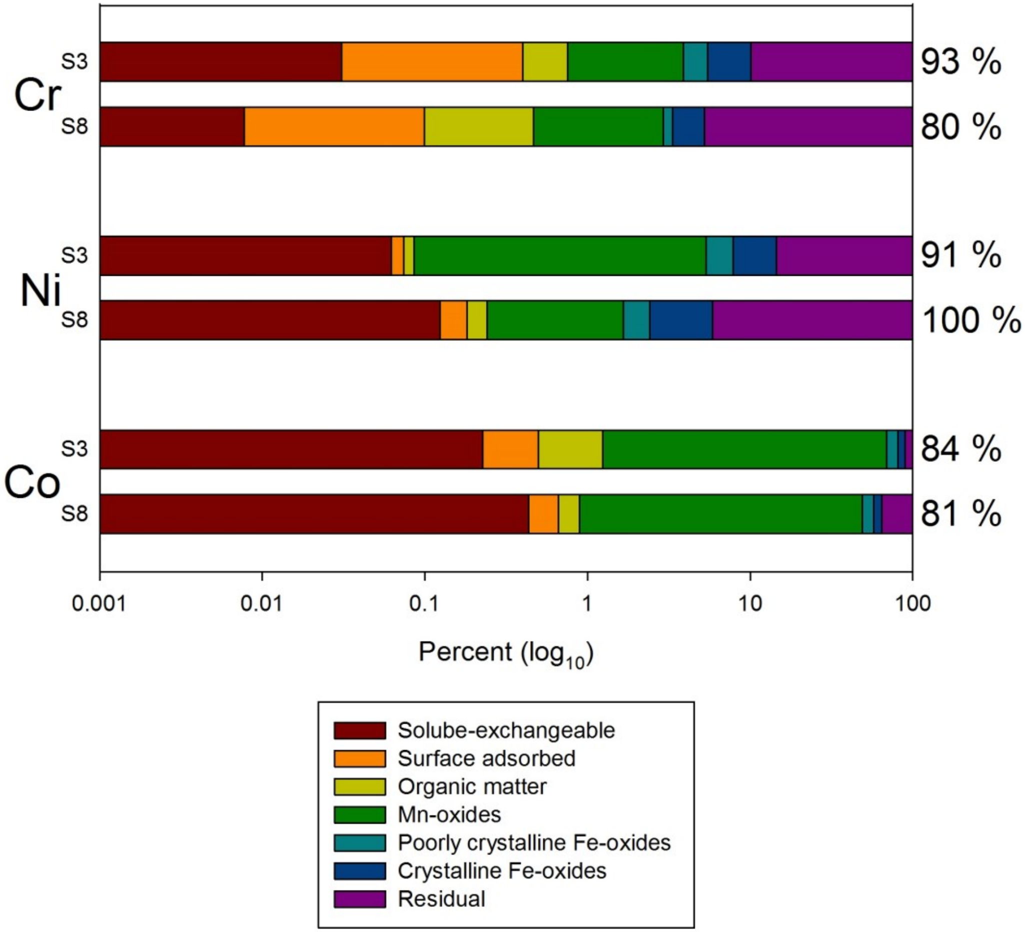


Fig 3. Percentage of chromium, nickel and cobalt found in seven soil fractions following selective sequential extraction (see Table 1) for serpentinite soils in the vicinity of Ranau, Sabah (Malaysian Borneo). Percentage recovery (in relation to total determination by XRF) is noted on the right-hand-side of the figure



APPENDIX

Table A1. The concentration of trace elements (µg g^{-1}) in serpentinite rocks and soils from Ranau, Sabah, Malaysia. bdl = below detection limits

	As	**Ba**	**Ce**	**Co**	**Cr**	**Cu**	**Ga**	**Hf**	**La**	**Nb**	**Ni**	**Pb**	**Rb**	**Sr**	**Th**	**U**	**V**	**Y**	**Zn**	**Zr**
R1	bdl	493	636	63	2743	20	bdl	6	38	32	1609	22	8	18	bdl	9	78	bdl	53	21
R3	bdl	466	616	64	2622	14	bdl	6	38	28	1840	23	7	9	bdl	9	62	bdl	59	16
R4	bdl	491	699	62	2641	25	bdl	6	38	37	1602	26	9	17	bdl	9	85	bdl	59	22
R7	bdl	552	600	61	2781	25	bdl	6	39	36	1658	24	9	19	bdl	9	84	bdl	51	22
Mean ± SD	-	501 ± 36	638 ± 43	63 ± 1	2697 ± 77	21 ± 5	-	6 ± 0	38 ± 1	33 ± 4	1677 ± 111	24 ± 2	8 ± 1	16 ± 5	-	9 ± 0	77 ± 11	-	56 ± 4	20 ± 3
S1	3	bdl	176	136	13929	54	3	4	25	10	1675	bdl	3	bdl	bdl	9	134	bdl	89	54
S3	2	bdl	159	122	14720	45	3	5	21	9	2237	bdl	2	bdl	bdl	9	189	bdl	88	14
S4	bdl	80	244	146	16381	67	5	5	22	12	1573	bdl	2	bdl	bdl	9	240	bdl	75	21
S5	2	bdl	144	112	14029	52	8	4	21	12	850	bdl	2	bdl	bdl	9	357	bdl	68	30
S6	bdl	29	237	167	19025	49	3	5	21	11	4753	bdl	3	bdl	bdl	9	205	bdl	139	16
S7	bdl	136	295	127	17233	49	5	4	23	15	1219	bdl	3	bdl	bdl	9	277	bdl	79	20
S8	4	597	523	35	2427	55	8	6	28	29	865	16	32	6	bdl	9	132	bdl	86	62
S10	1	158	319	114	15807	59	8	5	23	17	1311	bdl	3	bdl	bdl	9	279	bdl	85	30
S12	3	201	332	93	11277	26	6	5	23	18	972	bdl	4	bdl	bdl	9	238	bdl	71	30
S13	4	557	506	46	2828	33	10	6	26	28	1418	18	40	22	bdl	9	120	bdl	80	96
Mean ± SD	3 ± 1	251± 230	294 ± 133	110 ± 42	12766 ± 5736	49 ± 12	6 ± 3	5 ± 1	23 ± 2	16 ± 7	1687 ± 1156	17 ± 1	9 ± 14	14 ± 11	-	9 ± 0	217 ± 76	-	86 ± 20	37 ± 26

Table A2. Correlation coefficients between elements in serpentine soil samples in of Ranau, Sabah (Malaysian Borneo). Significant correlations ($p < 0.01$) are marked in bold

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Co	Cr
TiO_2	-0.07											
Al_2O_3	-0.44	**0.80**										
Fe_2O_3	**-0.94**	0.04	0.46									
MnO	-0.63	-0.32	0.18	**0.80**								
MgO	0.23	-0.54	-0.46	-0.06	0.32							
CaO	**0.81**	-0.09	-0.26	-0.75	-0.53	0.34						
Na_2O	**0.82**	0.05	-0.27	-0.71	-0.38	0.42	0.60					
K_2O	**0.87**	0.11	-0.09	**-0.83**	-0.62	0.06	**0.91**	0.61				
P_2O_5	0.20	0.22	0.31	-0.13	-0.23	-0.38	0.42	-0.06	0.51			
Co	-0.58	-0.20	0.37	0.66	0.61	-0.10	-0.23	-0.59	-0.29	0.44		
Cr	-0.73	-0.08	0.46	**0.80**	0.67	-0.22	-0.42	-0.70	-0.47	0.37	**0.96**	
Ni	-0.15	-0.55	-0.17	0.30	0.54	0.60	0.18	0.06	-0.12	0.04	0.59	0.47