

Mineralogical and Geochemical Characteristics of Serpentinite-Derived Ni-Bearing Laterites from Fars Province, Iran: Implications for the Lateritization Process and Classification of Ni-Laterites

S. Rasti, M. A. Rajabzadeh

Abstract—Nickel-bearing laterites occur as two parallel belts along Sedimentary Zagros Orogenic (SZO) and Metamorphic Sanandaj-Sirjan (MSS) petrostructural zones, Fars Province, south Iran. An undisturbed vertical profile of these laterites includes protolith, saprolite, clay, and oxide horizons from base to top. Highly serpentinized harzburgite with relicts of olivine and orthopyroxene is regarded as the source rock. The laterites are unusual in lacking a significant saprolite zone with little development of Ni-silicates. Hematite, saponite, dolomite, smectite and clinocllore increase, while calcite, olivine, lizardite and chrysotile decrease from saprolite to oxide zones. Smectite and clinocllore with minor calcite are the major minerals in clay zone. Contacts of different horizons in laterite profiles are gradual and characterized by a decrease in Mg concentration ranging from 18.1 to 9.3 wt.% in oxide and saprolite, respectively. The maximum Ni concentration is 0.34 wt.% (NiO) in the base of the oxide zone, and goethite is the major Ni-bearing phase. From saprolite to oxide horizons, Al_2O_3 , K_2O , TiO_2 , and CaO decrease, while SiO_2 , MnO , NiO , and Fe_2O_3 increase. Silica content reaches up to 45 wt.% in the upper part of the soil profile. There is a decrease in pH (8.44-8.17) and an increase in organic matter (0.28-0.59 wt.%) from base to top of the soils. The studied laterites are classified in the oxide clans which were derived from ophiolite ultramafic rocks under Mediterranean climate conditions.

Keywords—Iran, laterite, mineralogy, ophiolite.

I. INTRODUCTION

Ophiolite rock-derived Ni-laterites have attracted the researchers due to their scientific aspects such as understanding the supergene processes that acted on the surface of the Earth [1], [2] as well as their economic importance [3]-[7]. These deposits are developed on ultramafic rocks under tropical or subtropical conditions throughout earth history [4], [8]-[14]. At present, nearly 25% of the Earth's continental surface is located in tropic regions, and then is climatically favorable for the formation of laterites [15]. Over 60% of nickel resource in the world and nearly 40% of the world's annual nickel production comes from the laterites [16]. Abundance of ophiolite sheets in Iran necessitates the investigation on lateritization in ophiolite

belts. Two Ni-bearing laterite belts trending NW-SE have been recently discovered in Bavanat region. These soils occur discontinuously along SZO and MSS petrostructural zones, Fars Province, south Iran. These laterites with varying size are the only known Ni-bearing soft rocks in the country. The ophiolite rocks are regarded as fragments of the Neo-Tethyan oceanic crust and upper mantle which were exposed on continental margin of the Central Iran block during collision between Afro-Arabian and Iranian micro-plate in the Late Cretaceous. The present study deals with a preliminary evaluation of field observation associated with mineralogical and geochemical investigation of Ni-bearing soils. This work helps us to get detailed information on the lateritization process and Ni enrichment mechanism during the serpentinite weathering.

II. GEOLOGICAL SETTING

Two Ni-bearing laterites in the studied region are named northern and southern belts that extend 180 and 450 km² respectively. These laterites were derived from ultramafic ophiolite rocks. The ophiolite peridotites would have likely been partially serpentinized by the hydrothermal reaction of oceanic water with the mantle rock as they moved upwards through the forearc/arc lithosphere prior to their final emplacement in their current crustal tectonic position. The ophiolite was derived from a fast spreading oceanic ridge linked to a northeast-dipping subduction zone associated with the initiation of immature island-arc tholeiitic lavas at the upper levels of the ophiolite. The ophiolite rocks are thrust over limestone of Bangestan Formation of Early Cretaceous and are conformably overlain by shallow-water marly limestone of Late Cretaceous, indicating the emplacement of ophiolite on the Iranian microcontinent which took place in the Maastrichtian [17]-[21]. Two major faults including Jian Fault at northern and Jovakan Fault at the southern borders separate the study region from the MSS and SZO, respectively (Fig. 1).

Mohammad Ali Rajabzadeh is with Department of Earth Sciences, Shiraz University, Iran (phone: +989123873933, fax: +987132284572, e-mail: rajabzad@susc.ac.ir).

Soqra Rasti is with Department of Earth Sciences, Shiraz University, Iran (phone: +989171356164, e-mail: rasti.s@shirazu.ac.ir).

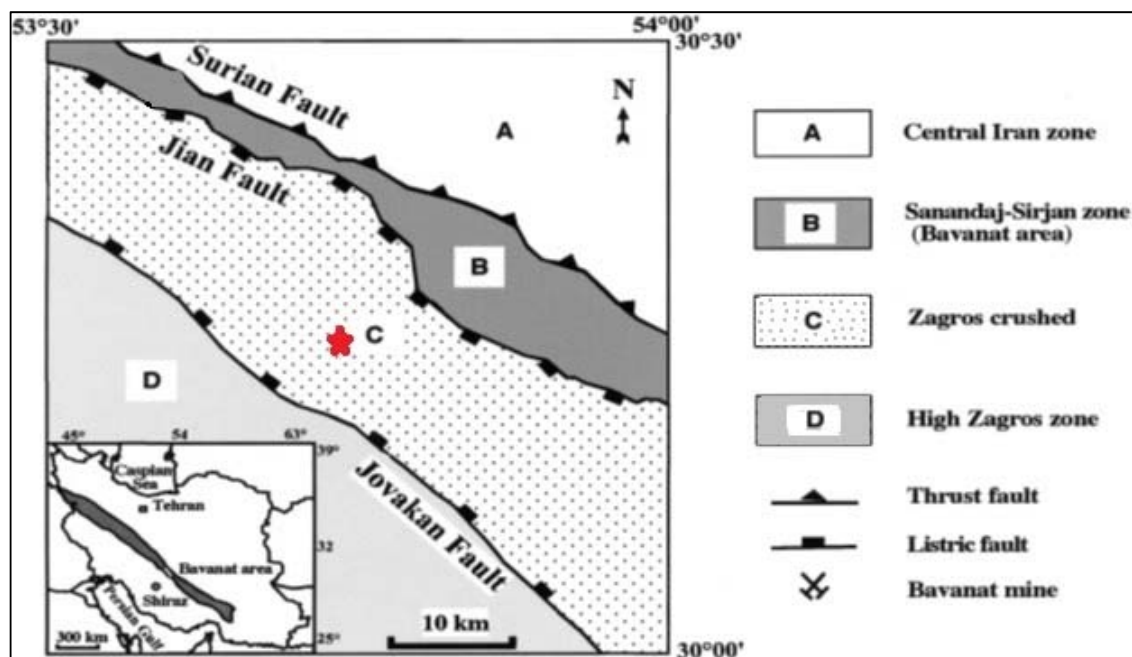


Fig. 1 Map showing the petrostructural units of the Bavanat region (after [22]) and location of the studied area

III. SAMPLING AND ANALYTICAL TECHNIQUES

Sampling was carried out through lateral and vertical profiles in order to obtain representative samples from different zones including protolith, saprolite, clay, and oxide horizons in laterite. To achieve an approximate statistical homogeneity, samples of a minimum 2 kg weight were collected and were dried. The samples were impregnated with a polyester resin mix and polished using successively finer diamond paste. Polished thin sections of all samples were examined under reflected light microscope. Mineralogical data were completed by X-Ray Diffraction (XRD) method at Kansaran Binalod Laboratories, Iran. Major and minor-trace elements were determined, using X-Ray Fluorescence Spectrometry (XRF) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at Zarazma Mineral Studies Laboratories, Iran. pH value of soils was determined using a glass electrode after 25 g of soil which had been stirred well in 62.5 ml distilled water for about 1 h. Organic matter in the studied soils was also determined, following a wet oxidation method (Walkley-Black), using 1 N $K_2Cr_2O_7$ solution. The remaining dichromate was titrated with ferrous sulphate [23].

IV. LATERITE PROFILES

Vertical profiles of the laterite in Bavanat region comprised of four different zones from base to top of the studied soils, including (a) protolith; (b) saprolite; (c) clay-rich laterite and; (d) oxide-rich horizons (Fig. 2).

Protolith horizon: The weathered protolith is dark-green highly serpentinitized harzburgite containing relicts of olivine and orthopyroxene. Magnesite with white color occurs as narrow boxwork veinlets along joint planes and surrounds serpentinite fragments. Calcite veins and veinlets are also

found within this horizon and unlike in many modern deposits, are coincident with the weathering front and decrease upwards. Silica occurs as granular coarse grains in the veins and veinlets as well as in “isolated pockets” in serpentinite. These pockets with brownish to black colors are formed of tiny clusters and/or mineral aggregates with no feeders.

Saprolite horizon: This zone overlies the protolith with an irregular, but gradual contact. It is commonly developed along the gentle slopes and to a less extent in the highlands. It appears in mixed colors such as yellowish-green, grayish-yellow and grayish-green with varying thickness ranging from 1 to 5 m. The saprolite horizon is loose, porous and friable, containing different proportions of fine-grained groundmass (earthy saprolite) and coarse-grained fragments of 5–25 cm in diameter (rocky saprolite). These fragments of pale yellow ochre or a dark gray color show relict original fabric with concentric alteration zones in the matrix of soft serpentinite. The primary structure of the protolith can be partly observed in the lower part of the saprolite horizon where the rocky blocks are abundant. Minor limonite is found in this zone, but quartz may be abundant locally in the form of silica boxwork.

Clay horizon: This horizon is discriminated by a visible contact in color from the saprolite horizon. It is found in the flat relief with 1–7 m in thickness and brownish-red to brownish-yellow in color. This horizon is, soft, porous, and fine grained. Despite its position at top of the saprolite horizon, locally it grades downward to the serpentinite. This zone is characterized by a development of fractures which were filled by silica.

Oxide horizon: It lies at the uppermost level of the studied soils, directly over the clay horizon. This horizon is well preserved in the highland and commonly eroded away in the

deep slope. Constituent materials of this zone are soft and incoherent with reddish brown in color. The oxide zone is characterized by massive or colloidal textures including ferruginous concretions of variable diameters ranging from 1 to 5 cm. Silica veinlets in stockworks can be observed in the bottom of this horizon.



Fig. 2 Different horizons in a vertical profile of the studied laterites in Bavanat region

V. MINERALOGY

Mineralogical data of the laterites from bottom to top of the vertical profiles in Bavanat region showed a progressive transition in mineral type from the serpentine dominant to the Fe-oxyhydroxide dominant, with some sudden changes (like calcite and quartz) in some specific horizons. This trend indicates that hematite, saponite, dolomite, smectite, and clinocllore increase, while calcite, olivine, lizardite, and chrysotile decrease upwards. Microscopic observations in association with XRD data showed that serpentine, most likely lizardite with minor chrysotile, is the dominant mineral in the protolith horizon. Lizardite and chrysotile are characterized by a strip-like mineral shape. Olivine and orthopyroxene relicts are clear under microscope. Calcite and to some extent quartz are found as veinlets in irregular networks of fractures. Trace Cr-spinel grains are also observed as interstitial mineral phases (Fig. 3 (A)). Mineralogical data of saprolite horizon revealed that serpentine is the most abundant mineral in the lower part of this horizon and olivine and pyroxene are only slightly preserved. The serpentine is accompanied by goethite and hematite in the upper part of the saprolite horizon (Fig. 3 (B)). Clay horizon is dominated by clay minerals, mainly smectite and saponite with minor montmorillonite and chlorite. Minor goethite and hematite occur as fracture infillings. Quartz content in this zone is more abundant than saprolite horizon, Fig. 3 (C). The oxide horizon is characterized by a relatively simple mineralogy. It mainly consists of fine-grained iron oxide minerals, dominated by hematite and goethite, accompanied by minor dolomite and quartz (Fig. 3 (D)).

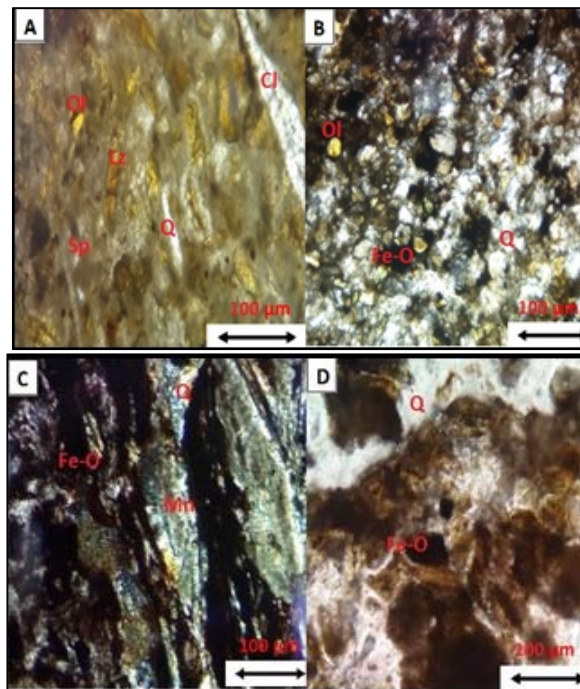


Fig. 3 Microphotographs of the laterite horizons from Bavanat region. (A): protolith, (B): saprolite, (C): clay and (D): oxide horizon. Sp: Serpentine, Lz: Lizardite, Ol: Olivine, Cl: Calcite, Q: Quartz, Mn: Montmorillonite and Fe-O: Iron oxyhydroxide

VI. GEOCHEMISTRY

Geochemical data of major, minor and trace elements are summarized in Table I (in average for each horizon). The distributions of major elements and some interesting trace elements through the vertical profile indicated that the protolith is characterized by a high concentration of Ca (8.2% CaO) and Si (34.8% SiO₂), coupled with a low concentration of Fe (7.99% Fe₂O₃) and Al (5.1% Al₂O₃). The Ni concentration of the bedrock is about 0.1% (NiO). The saprolite samples show a remarked decrease in Ca (avg. 6.44% CaO) and an increase in Al (avg. 7.1% Al₂O₃) and Si (37.9% SiO₂). The Fe (avg. 7.9% Fe₂O₃) and Ni (0.1% NiO) contents are similar to protolith. The clay zone samples exhibit a further decrease in Al (avg. 5.1% Al₂O₃), Fe (avg. 7.9% Fe₂O₃), Ca (avg. 6.4% CaO) and Si (avg. 36.4% SiO₂) compared to those of saprolite horizon. The average Ni concentration of the samples from clay zone is 0.17% (NiO), which is slightly higher than Ni in saprolite samples. In the uppermost horizon, oxide zone samples contain higher Fe (avg. 8.3% Fe₂O₃) and Si (avg. 45% SiO₂), but a drop in Al (avg. 4.9% Al₂O₃) and Ca (avg. 4.5% CaO) concentration. The Ni concentration of this horizon is 0.23% (NiO) that is higher than that of clay horizon.

In summary, Al₂O₃, K₂O, TiO₂, and CaO decrease, while SiO₂, MnO, NiO, and Fe₂O₃ increase from bottom to top of the laterite profiles. MgO content varies gradually from one horizon to another, characterized by an increasing trend from bottom to top of the different zones, for example MgO is 7.3

wt.% in lower border of saprolite zone while it is 18.1 wt.% in upper border of this zone. The maximum Ni concentration of the studied soils is 0.34 wt.% in the base of the oxide zone and goethite looks like to be the major Ni-bearing phase. The concentration of Cr shows a decrease from bedrock (1.5 % Cr₂O₃) upwards in oxide zone (avg. 0.44 % Cr₂O₃). Vanadium, cobalt, and manganese steadily increase upwards. SiO₂ content reaches 52.9 wt.% at the base of the oxide zone.

The ΣREE in the vertical profile varies in the range of 28.6 - 67.5 ppm. The ΣREE in the unaltered protolith is about 50.4 ppm. A slight increase of REEs is observed in the saprolite zone (58.8 ppm). The distribution pattern of normalized REEs [24] in each horizon indicated that the patterns are similar, characterized by enrichment in LREEs relative to HREEs.

Zones with Mn and Mg enrichment (clay zone) are characterized by a slight positive anomaly in Ce (Ce/Ce* = 1.1), but the deeper horizons (protolith and saprolite) and the upper zone (oxide zone) negative anomaly (Ce/Ce* = 0.9). Nearly all the horizons of laterite profile are characterized by a slight positive anomaly in Eu. Fractionation of the REEs is exemplified by the ratio of La/Lu. This ratio reaches up to 172.7 in the oxide zone (avg. 105.1 ppm). There are decrease in pH (8.44-8.17) and increase in organic matter (0.28-0.59

wt.%) from base to top of the soils.

Major elements are reported as wt.% and minor and trace elements are in ppm.

VII. DISCUSSION

Primary minerals in the ultramafic rock including olivine and pyroxene are the earliest minerals experiencing alteration when ultramafic rocks uplifted to the surface. Weathering of ophiolite ultramafic rocks under humid climate condition results in the development of Ni-rich ferruginous horizons. Mineral evolution during the lateritization depends on the nature of the primary minerals as well as environmental conditions. The pH and organic matter content play a significant role in the formation of different weathering products in the soil profile. At the presence of sufficient organic matter and low pH, Ni is highly mobile. Physicochemical characteristics, such as soil porosity-permeability, soil grain size and mineral type should not be ignored during the lateritization. Topographic factors, including the drainage pattern and relief may promote the weathering front to move deeper by lowering the water table.

TABLE I
GEOCHEMICAL DATA OF THE STUDIED SAMPLES FROM DIFFERENT HORIZONS OF NI BEARING LATERITES IN BAVANAT REGION

Zone	Al ₂ O ₃	MgO	Fe ₂ O ₃	CaO	Cr ₂ O ₃	SiO ₂	K ₂ O	MnO	Na ₂ O	As	Ba	Co
Oxide zone	4.94	13.16	8.26	4.48	0.44	44.97	0.14	0.08	0.063	6.6	58.1	75.43
Clay zone	5.13	16.06	7.98	6.39	0.58	36.43	0.21	0.15	0.055	9.1	47.3	77.30
Saprolite	7.15	13.3	7.89	6.44	0.4	37.96	0.89	0.11	0.130	3.3	55.7	73.73
Protolite	5.13	14.5	7.99	8.23	1.49	34.77	0.15	0.10	0.050	7.8	56.2	73.70
Zone	Cr	Cs	Cu	Hf	Li	Mo	Nb	P	Pb	Rb	S	Sc
Oxide zone	1216.1	1.3	23.3	1.05	21.1	1.69	6.06	149.2	8.66	8.67	179.5	12.00
Clay zone	1569.5	1.1	19.5	0.85	19.5	1.04	4.05	172.4	5.10	10.1	128.5	17.55
Saprolite	1104.6	2.1	38.3	1.53	22.1	1.53	5.00	232.5	8.66	30.6	88.1	19.46
Protolite	3737.1	0.9	20.1	0.79	16.0	1.55	4.70	213.1	7.00	9.2	99.4	17.1
Zone	Se	Sn	Sr	Ta	Te	Th	Ti	Tl	U	V	W	Y
Oxide zone	0.65	0.73	122.1	0.79	1.69	2.61	1896.6	0.50	0.68	66.3	38.16	8.20
Clay zone	0.51	0.55	225.1	0.56	3.16	1.87	2134.0	0.28	1.20	104.5	4.10	7.95
Saprolite	9.74	0.70	191.6	0.85	0.52	2.85	2510.3	0.21	0.73	90.6	8.35	11.86
Protolite	0.54	0.51	253.6	0.62	0.6	2.13	2400	0.14	0.60	97.0	14.81	10.8
Zone	Zn	Zr	Ni	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
Oxide zone	113.66	42.33	1781.3	13.0	16.3	1.49	9.56	1.79	0.40	1.69	0.26	1.90
Clay zone	63.00	26.51	1351.2	6.5	10.1	0.74	6.85	1.45	0.34	1.46	0.24	1.91
Saprolite	83.33	43.10	791.6	10.3	19.6	1.65	10.43	2.13	0.51	2.13	0.35	2.49
Protolite	70.00	28.10	826.0	9.0	16.0	1.44	9.90	2.16	0.57	2.10	0.35	2.57
Zone	Er	Tm	Yb	Lu	ΣREE	La/Lu						
Oxide zone	0.87	0.16	0.73	0.13	41.18	105.1						
Clay zone	0.86	0.16	0.85	0.14	31.40	46.4						
Saprolite	1.29	0.22	1.36	0.18	58.79	57.1						
Protolite	1.18	0.20	1.10	0.16	50.38	56.2						

The average values are reported.

Alteration of serpentine commences at supergene environmental conditions, and its alteration path may be diversified depending on these conditions [25]. The presence of this mineral in association with clay minerals in studied laterites indicates that the serpentine alteration occurred where the water table is high or drainage is poor [26]. This alteration

took place in a mildly alkaline environment by an ionic exchange reaction between the serpentine and weathering solution. By this reaction, Ni replaces part of the octahedral Mg in serpentine [25], [27]. This evidenced by the higher Ni value in saprolite horizon than protolith zone in the study area. The lack of garnierite in the study area is explained by a

number of geological and environmental factors. The very low Ni concentration (avg. 826 ppm) in protolith did not provide the abundant Ni source of formation the garnierite. The rainforest climate condition was not favorable for Ni transportation and accumulation in the weathering solutions. In addition, there may be insufficient joints and fractures in the source rock from Bavanat region. These features act as the pathways for the percolation of Ni-saturated solution and the precipitation space for garnierite in the lower part of the laterite profile [28].

In the lower part of the study profile (clay horizon), part of the leached Ni fixes in clay minerals, as indicated by the presence of saponite. Under an oxidized and more acidic condition (oxide horizon), serpentine directly altered to Fe-oxyhydroxide (e.g., goethite). Mineralogical evidence of the studied samples shows that serpentine coexists with hematite and goethite. In surficial environment with high OM and low pH, hematite is more stable than goethite during lateritization, and goethite may be turned into hematite by dehydration [11], [25]. In this case, the leached Ni fixes in goethite due to its large surface area and open channel structure [29], or can be adsorbed by organic matter [30]. The strong positive correlation among SiO_2 , Fe_2O_3 , MgO , and Al_2O_3 in the weathering profiles indicates the high immobility of iron in weathering profiles [31], [32].

Depletion in HREEs rather than LREEs suggests that some of HREEs have been removed from studied soils during weathering. The similarity of REEs diagrams indicates the homogeneity of the laterite horizons in terms of the source and origin of REEs in Bavanat region. The negative correlation between Ce/Ce^* and Fe values indicates that Fe oxides promote Ce oxidation in the soil horizons.

On the basis of field observation and mineralogical and geochemical data, we classify the studied laterites in the oxide clan, where most the nickel is included in the iron oxides (goethite and hematite) with minor quantity adsorbed on the clay minerals (mainly smectite). The following evolutionary model is proposed for the laterite development in the Bavanat region.

A. Occurrence of Protolith Horizon

Subsequent to the emplacement of ophiolite ultramafic rocks on the continental margins in the Late Cretaceous, they were exposed to extensive weathering, and the formation of laterite deposits had been started under tropical rainforest conditions (probably in the Late Miocene). Protolith, the lowest horizon of the laterite profiles, indicates the early stages of weathering. The other horizons were transformed of that during advanced stages of the lateritization.

B. Saprolite Development

Saprolite can be regarded as the initial stage product of lateritization. Generally weathering begins along joints and faults, where the excess surface promotes the hydrolysis and oxidation of primary minerals of the protolith. According to the soil porosity-permeability, the weathering front moves deeper by lowering the water table. Soft saprolite is formed

where the saprolite is destroyed completely by further weathering processes over the hard saprolite (comprised mainly of rocky fragments). The Ni enrichment effect is uncertain at this stage because the weathering degree is relatively weak and inhomogeneous [15].

C. Clay Horizon Development

Clay horizon develops when the weathering front goes downward and most blocks or fragments of the protolith are greatly destroyed by the oxidation and hydrolysis. Serpentine is altered to clay minerals, where the drainage condition was poor. In this stage, the leached Ni in solution substitute Mg of serpentines by the ion exchange reactions. A remarkable amount of Ni-rich clay minerals is preserved.

D. Oxide Horizon Development

In progressive regional uplift setting, the weathering front passes the formation field of the hematite and goethite. During this stage, oxide minerals occur at the expense of released Fe from olivine by rock-water progressive interaction. Ni^{2+} released from the primary minerals adsorbed by the goethite and promotes the Ni concentration in the oxide samples to around 2000 ppm.

VIII. CONCLUSION

- 1) Widespread weathering of serpentinite created Ni-bearing laterites with four specific horizons, including protolith, saprolite, clay, and oxide zones. Different weathering products were formed under various pH and organic matter content from bottom to top of the soil profile.
- 2) Mineral assemblages change from the silicates dominant (mainly serpentine and olivine) to the Fe-oxyhydroxide dominant (mainly goethite and hematite) ones from bottom to top of the soil profile reflecting mineral evolution during the lateritization process.
- 3) The geochemical data shows a typical laterite pattern, in which Al_2O_3 , K_2O , TiO_2 , and CaO are depleted toward the top of the profile, whereas SiO_2 , MnO , NiO , and Fe_2O_3 increase. The highest Ni concentration (avg. 2700 ppm) is shown in the oxide horizon samples.
- 4) Protolith, saprolite, clay and oxide horizons are developed successively by multistage process during progressive lateritization.
- 5) Bavanat laterites can be classified as oxide laterite type.

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