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# Cobalt in the regolith upon Nui Nua ultramafic Massif

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### ABSTRACT

*Cobalt (Co) Metal plays an increasingly important role in the battery and engine manufacturing industry for electric cars. Previously most of Co was mined as by-product in copper ore deposits in Central Africa. Recently, the proportion of Co extracted from other sources such as weathering-derived mines on ultramafic rocks is increasing. In Vietnam, Cobalt has been discovered in Cu-Ni ore deposits in the Northeast and Northwest Regions. The literature shows that cobalt is found in small amounts in ultramafic rocks. During the weathering process of ultramafic rocks, Co ions will be priority adsorbed in the hydroxide colloids of Mn and Fe (goethite and asbolan). In the regolith upon Nui Nua Masif, Ni content increased dramatically (several times) from 0.19% in bedrocks up to 1% in some locations, while cobalt content just increased only slightly (from 0.02% in bedrock to 0.05 regolith, rarely up to 0.1%). The results of the previous analysis of weathered crust samples of ultramafic rocks of Nui Nua massif by several authors show that, unlike Ni which is presented in both silicate minerals and Fe-Mn oxide/hydroxide, cobalt ions tend to be concentrated in Fe-Mn oxides/hydroxides. Our SEM analyses combined with EDS show some remarkable results: the Co content in some specific minerals is quite high from 1.12÷4.67% (denominator). This is only a preliminary result and it is necessary to conduct more work to further detailed studies defining the Co potential in weathering products of ultramafic rocks of Nui Nua massif as well as in the areas where other ultramafic rocks are developed. Recently, research confirmed that there is a significant Co-Ni occurrence discovered in Mau Lam Valley (Southwest of Nui Nua Massif).*

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## 1. Introduction

Cobalt (Co) is a metal that has been known and exploited by humans for several hundred years but has only received much attention in recent times due to its applications to make materials used in manufacturing electric motors and batteries. Currently, along with the development of mobile phones, there is a strong trend of switching from cars using conventional fuels (petroleum) to using electric energy, the demand for Co metal is skyrocketing to satisfy the requirement of the field of manufacturing batteries and motors for electric cars with the current annual demand of hundreds of thousands of tons of Co metal and will reach millions of tons in the near future (Shedd, 2018).

It is known that in the territory of Vietnam, Co occurrences have been found in the bodies of Ni-Cu sulfide at Ban Phuc (Son La), Suoi Cun, and Ha Tri (Cao Bang). Cobalt is also found in Copper ore bodies in An Luong (Yen Bai) and in Titanium ore in Cay Tram deposit (Thai Nguyen). In addition to Co ore found in endogenous mines (Cu-Ni-Co sulfide ores), there are also Ni-Co ores of exogenous origin distributed in the regolith on

ultramafic rocks in Cao Bang and Song Da areas. Especially, a large amount of Co has been found in the sediments around the Nui Nua ultramafic massif. Investigation results of Geological Division 401 (Dao, 1983) showed that Co reserves in Nui Nua area (Thanh Hoa province) may reach up to tens, even hundreds of thousands of tons. Despite such value, this type of ore until recently has not been got enough evaluation to be exploited.

## 2. General description of Nui Nua ultramafic rocks

Nui Nua ultramafic rocks are exposed about 20 km in the southwest of Thanh Hoa city in Nong Cong and Trieu Son districts with a length of about 15 km, a width of 1÷7 km and a total area of nearly 60 km<sup>2</sup> (this is the largest ultramafic massif in Vietnam). The surrounding rock is mainly metamorphic sediments of Nui Nua Formation ( $P_2-T_1mn$ ) with the main composition of quartz-sericite schist, green shale, shale and coarse-grained sediments of Dong Do formation ( $T_3n-rđđ$ ). Much of the northeastern and southwestern edges of the massif are covered by Quaternary sediments (Figure 1a).

Nui Nua massif is cut through by many fault systems. There are many mafic rocks that cut

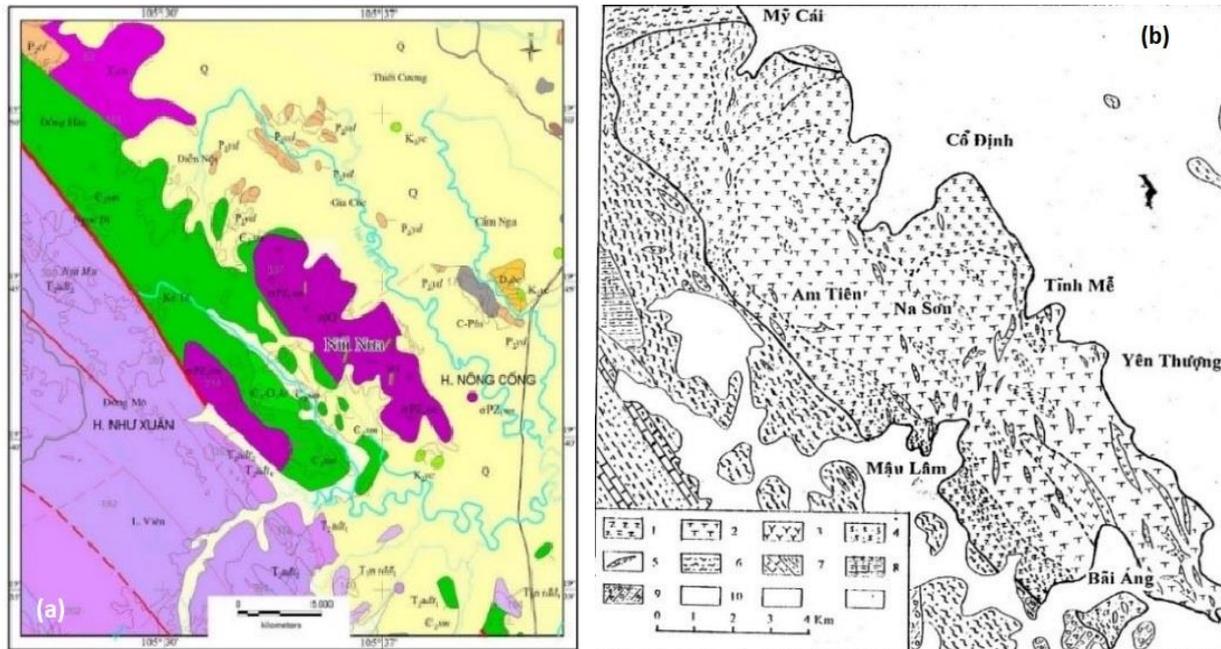


Figure 1. (a) Geological sketch of Nui Nua area, Thanh Hoa (Data from geological map 1:200,000 groups of Ninh Binh-Thanh Hoa maps); (b) Petrographic Sketch of Nui Nua ultramafic massif (Dao, 1983; Giang and An, 1998). Notes: 1- Apodunnite, 2- Apoharbuagite, 3- Apolerhzolite, 4- Serpentinite, 5- Diabas Dike, 6- Nui Nua Formation rocks ( $P_2-T_1nn$ ), 7- Dong Trau Formation rocks ( $T_2adt$ ), 8- Sedimentary rocks of the Qui Lang Formation ( $T_1-2ql$ ), 9- The rocks of the Dong Do Formation ( $T_2n-rdd$ ), 10- Quaternary sediments (Q).

through to form dike bodies, especially south and southeast of the massif. These ultramafic rocks are strongly fractured, especially at the margins, which are compressed and fragmented to form thin lamelars.

The ultramafic rocks exposed at Nui Nua massif are mainly apodunite and apoharzburgite (Figure 1b), all of these rocks are strongly metamorphosed (serpentinization, talcization, etc.); The fairly common occurrence of white asbest (chrysotil) veins in the exposed bedrock in southeast areas is one of the manifestations of the serpentinization process here (Figure 2b). Under the optical microscope, the apodunite still retains the remnants of olivine grains very clearly (This serpentine type accounts for 85÷95% of rocks composition), in addition, there are remnants of pyroxene grains (5÷10%); apoharzburgite has olivine remnants (mostly turned into serpentine, 50÷59%), pyroxene remnants (15÷20%). Secondary minerals include cromspinel, and ore minerals (ilmenite and magnetite). Secondary minerals include chlorite and talc.

In the Nui Nua ultramafic massif, many chromite veins and pots have been found with sizes ranging from a few tens of centimeters to several meters. Chromite grains with sizes

varying from a few mm to more than 1 cm. This is the main source of chromite placer deposits around Nui Nua Range.

Research results of Dao (1983) show that the dispersion rings of Ni and Co have a narrower distribution area, in which the dispersion rings of Ni are mainly southwest of Nui Nua, from Mau Lam valley towards Bai Ang area and a little in the area from My Cai to Co Dinh. The scattered rings of Co are usually smaller and shorter in size, concentrated on the Northeast slope (Tinh Me area and Southwest Co Dinh). In Nui Nua ultramafic rock, the relationship between Ni and Co is quite close (correlation coefficient  $R = 0.7$ ), while the relationship between Ni and Co and Cr is less tight (the coefficient between Ni and Cr is 0.5 and Co-Cr is 0.53). The published data (Giang and Dung, 2020) confirmed that Ni and Co substitute for Fe and Mg in olivine/pyroxene and their metamorphosed product (serpentine), while Cr mainly exists in the form of chromite ( $\text{FeCr}_2\text{O}_4$ ).

### 3. Material and Method

The Nui Nua ultramafic massif has outstanding geological value and is considered by many geologists to be a remnant of ancient

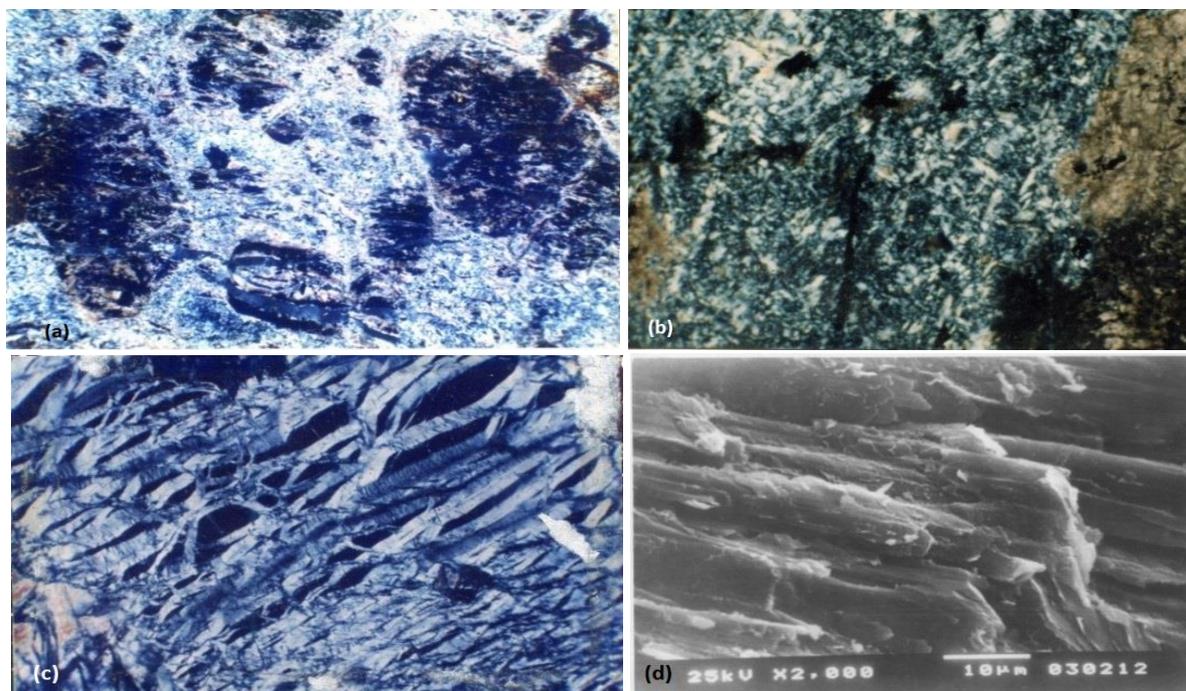


Figure 2. Some photos of serpentinized ultramafic rock at Nui Nua. (a)- Olivine remnants in apodunite Nicol + , x70; (b)- Antigorite, Nicol + , x70; (c)- Lizardite, Nicol + , x70; (d)- SEM image of Serpentine, 2000X.

oceanic crust (ophiolite). In addition, the Nui Nua ultramafic rocks are also related to some types of minerals, especially Cr and Ni. Therefore, these rocks have been studied by many geologists. There are some works on the Cr-Ni occurrence in the regolith upon Nui Nua massif such as An and Huyen (1979), Dao (1983), Giang and An (1998), Dang et al. (2020), Giang and Dung (2020).

In order to contribute to a better understanding of the material composition as well as distribution characteristics of Co in Nui Nua area to serve the exploration and exploitation of this metal, last year, the authors conducted a field trip, collected additional samples for analysis, and initially assessed the concentration as well as potentials of Co ore in regolith on the Nui Nua ultramafic massif. A total of 24 samples were collected in the variable weathering profiles. Among them, 12 typical samples were selected for analysis by X-Ray diffraction analysis (XRD) to determine regolith mineralogical composition. The Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS) equipment has been used to define the mineralogical composition as well as the content and distribution pattern of Cr, Ni and Co in the

major minerals (smectite clay group, goethite and asbolan) of Nui Nua ultramafic regolith. The XRD analytical samples were sent to the Lab of the Geological Analytical and Experiment Center of Minerals and Geological Survey of Vietnam. The SEM/EDS analyses were carried out in the SEM Lab of Hanoi University of Mining and Geology.

#### 4. Result and Discussion

##### 4.1. Generalizing characteristics of regolith on Nui Nua massif

Nui Nua ultramafic massif with an exposed surface area of more than 60 km<sup>2</sup>, has undergone a long process of weathering and erosion for tens of millions of years, creating a diverse weathering crust with different thickness depending on the weathering conditions. current relief. According to the research results of An and Giang (1997), Giang and Dung (2020), the weathered crust in this area has complete (mature) and eroded (incompleted) profiles. The complete profile is typical for relic weathering crust, distributed in the leveled surface with elevations from 400÷450 m in the northwest part of the block, around Na Son and Am Tien areas (Figure 3a).



Figure 3. Some pictures of weathering profile on Nui Nua ultramafic rocks: (a) The weathering profile riched in iron at Am Tien area, (b) The weathering profile with a thin thickness at the Serpentin mine, (c) The weathering profile with a thick thickness develops on the mafic dike in the Bai Ang area, (d) The delluvium containing chromite placer in the My Cai area.

In addition to the complete profile, in the regolith on Nui Nua massif, there is also a very common type of eroded (immature) profile with the top zone being a silt-clay zone typical for the erosion weathering crust, in which the strongly eroded crust (with thin-to-medium thickness) occupies the largest area of regolith on Nui Nua massif. They are distributed in places where the topographic surface has a medium level of

dissection (small mountain peaks and slopes with tilt angle < 45° (Figures 3b,c).

The authors conducted XRD analysis to determine the mineralogical composition of some typical samples of regolith on Nui Nua ultramafic Massif (Figure 4).

The results of determining the mineralogical composition of regolith on Nui Nua ultramafic rocks are shown in Table 1.

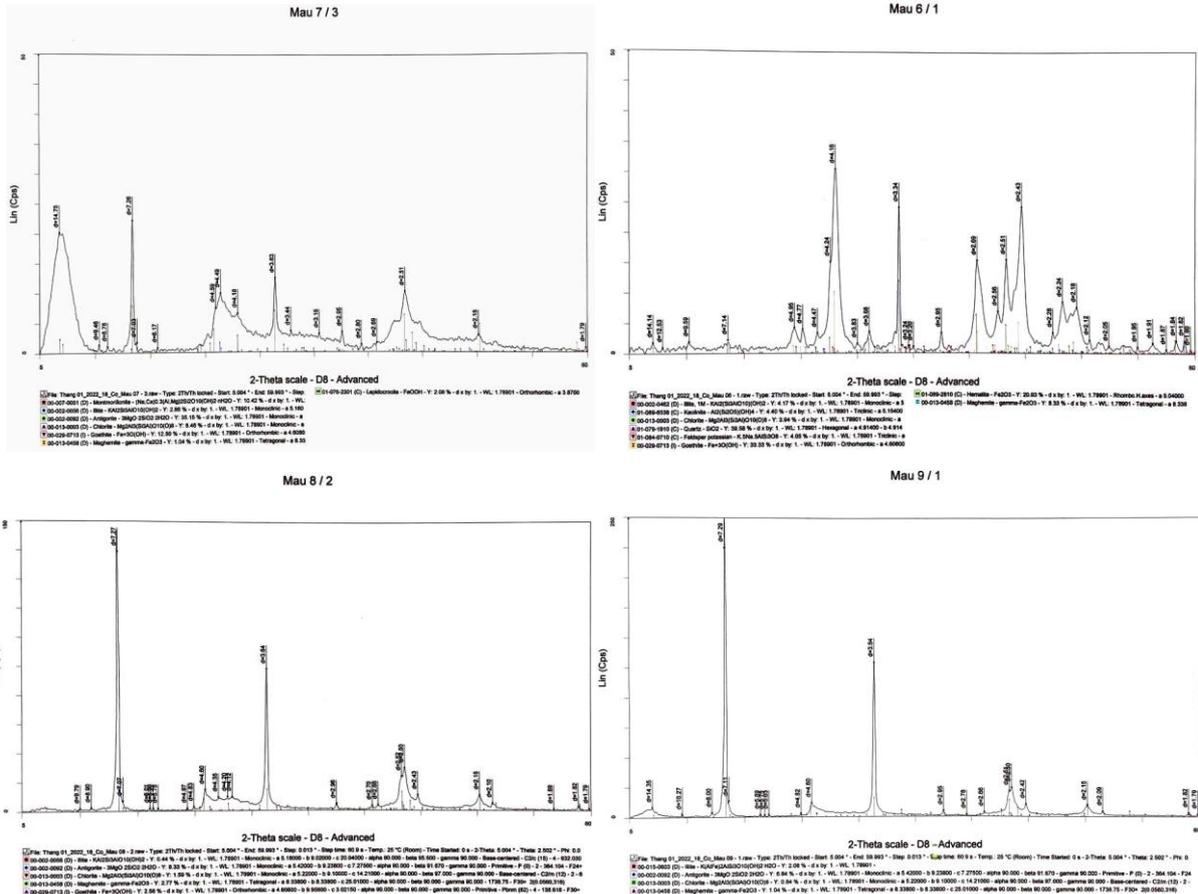


Figure 4. Rontgen diffraction diagrams of some typical samples of weathering crust (regolith) on ultramafic rocks in the Nui Nua area.

Table 1. Mineral composition of XRD analysis samples in the Nui Nua area.

N <sup>o</sup>	Sample Name	Variable mineral Composition (~%)								
		Montmo÷rillonite	Illite	Anti÷gorite	Chlorite	Quartz	Goethite	Maghemite	Absbolan/psilomelan	Other minerals
1	6/1	-	2÷4	-	4÷6	14÷16	58÷60	6÷8	≤ 1	7% He; Fel
2	7/3	47÷49	1÷3	28÷30	4÷6	-	4÷6	4÷6	1÷3	-
3	8/2	-	÷	84÷86	4÷6	-	-	6÷8	-	-
4	9/1	-	2÷4	81÷83	4÷6	-	-	6÷8	-	-
5	11/1	56÷58	4÷6	4÷6	18÷20	-	-	-	-	9% Am; Fel
6	TN 04	6÷8	4÷6	9÷11	4÷6	8÷10	16÷18	-	39÷41	3% Am

Note: He-hematite, fel-Feldspar, Am-amphibole.

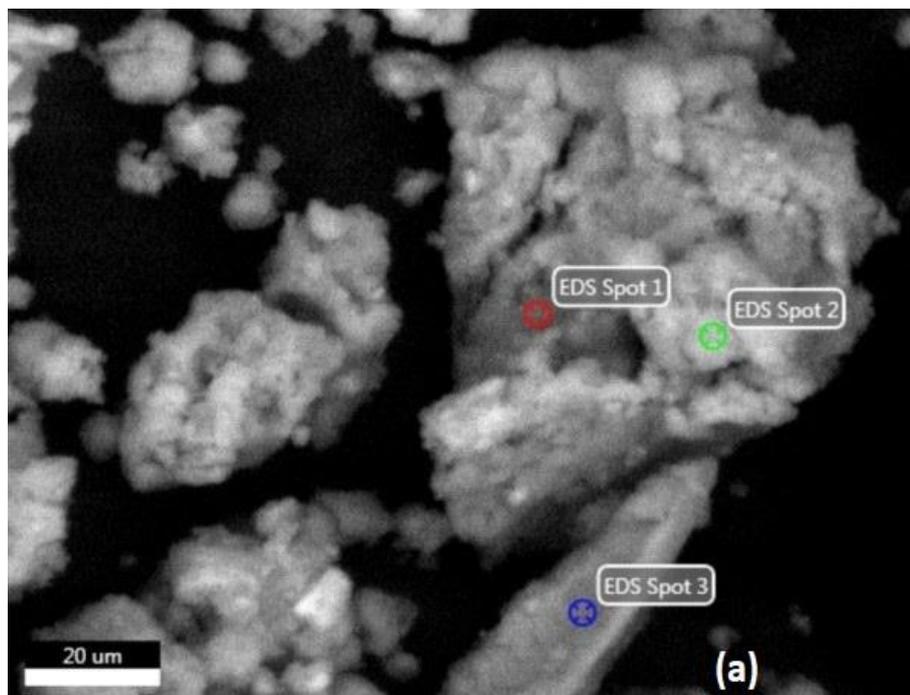
#### 4.2. Distribution pattern of Co in regolith on Nui Nua ultramafic massif

Research results of several published authors (Brand et al., 1998; Butt and Cluzel, 2013; Golightly, 2010) show that, during the weathering of ultramafic rocks, Ni ions when released from primary minerals, partly will participate in the formation of secondary silicate minerals such as smectite clays (nontronite/saponite), partly in the lattice cell or adsorbed by Fe hydroxide (goethite) while Co ions will be priority adsorbed in the hydroxide colloids of Mn. This rule can also be applied when studying the formation process of Ni and Co accumulations in regolith/sediments in the Nui Nua area. Initial research results show that during the weathering of ultramafic rocks of Nui Nua massif, Co and Ni are liberated from primary minerals (serpentine minerals, magnetite, chromite, etc.), a considerable part of Ni will go into the remnants of weathered silicate minerals (nontronite/saponite clay group), an important part of Ni is adsorbed in Fe hydroxides (with relatively large content in the regolith and sediments) and Mn hydroxide (with relatively low content).

As a result, Ni is dramatically enriched in in-situ weathering products and transported down the surrounding valleys (Ni content can be up to

several times that in bedrock). As for the Co ion after being released, it hardly participates in the structure of the secondary silicate minerals but is adsorbed in the colloids, due to its high affinity for Mn, it will preferentially adsorb more in the Mn colloids (pre-colloidal of asbolan and psiomelan) compared with colloidal iron. The results of the analysis of Co content in samples in the Nui Nua area and correlation with Mn content are completely consistent with this rule. The results of some published research (Brand et al., 1998; Butt and Cluzel, 2013; Golightly, 2010) show that both Ni and Co elements are significantly enriched during the weathering process, but Ni tends to be concentrated in the lower part of the cross-section. Nickel content increased from 0.3% in bedrock to 1.5÷4% in fractured rock and weakly weathered zones and decreased to 0.8÷1.5% in upper zones. The Co content tends to increase in the middle and high parts of the section, in the limonite zone, the Co content increases from 0.01 in the bedrock up to 0.1÷0.2%.

As above mentioned, to better understand the distribution of Co in the minerals of the regolith, the samples in the regolith of Nui Nua ultramafic rock were also analyzed by the EDS method to determine the distribution characteristics of some specific elements. The results are illustrated in Figures 5÷7.



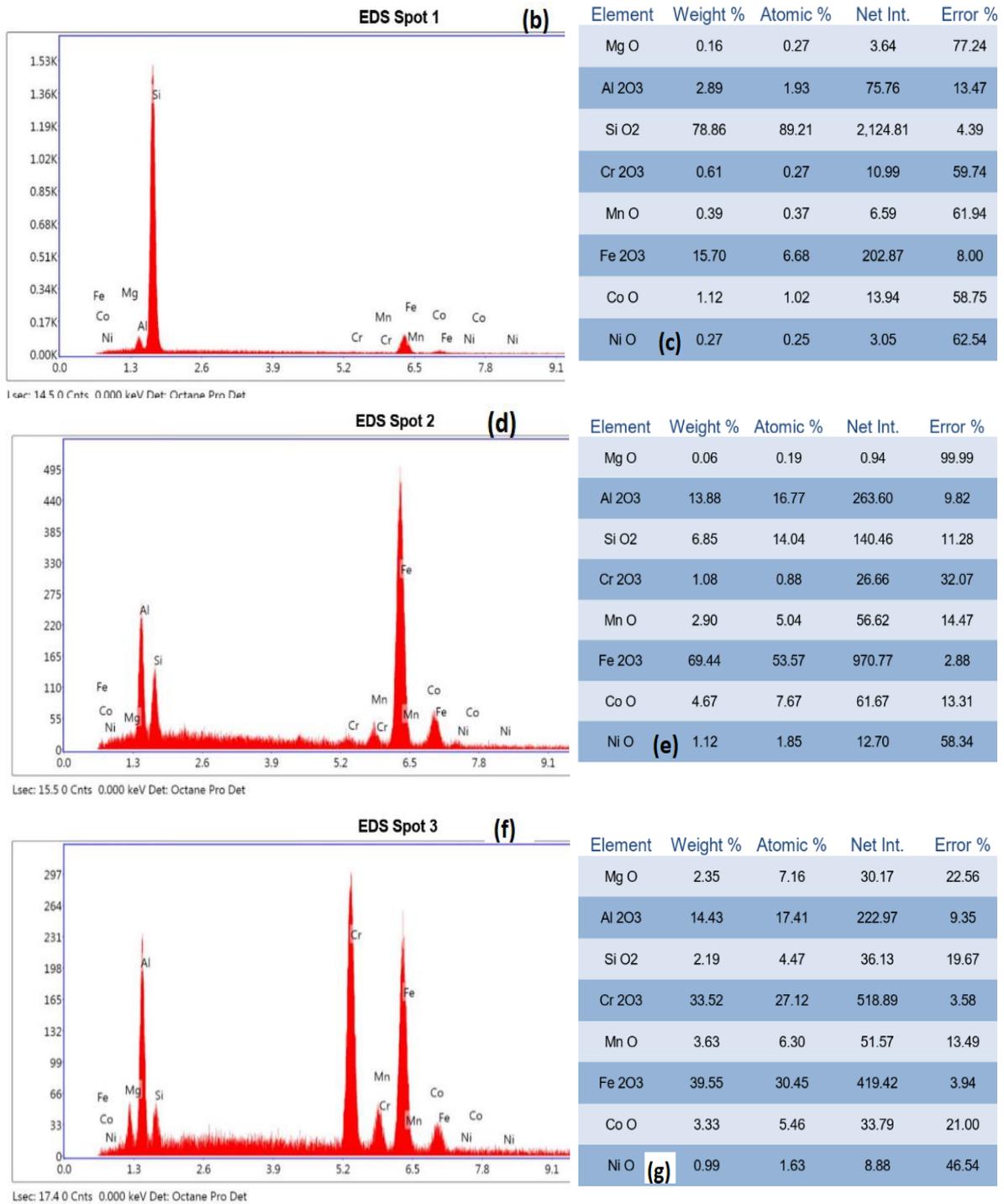


Figure 5. SEM/EDS analysis results of the samples from strongly weathered ultramafic rocks at outcrop 6 near Am Tien top hill. (a)-SEM Image of sample NN 6.1: Serpentine is strongly weathered collected in the profile near Am Tien area: chromite grains (chrompicotite) have elongated rods (in the lower right corner) and saponite/nontronite clay particles (grains with irregular shape). The locations of the EDS analysis points are marked in the image.

The boxes are the EDS plots of the shot points (left) and the results of the EDS analysis of that point (right). Point 1: Si-Fe colloids (b,c); Point 2: Laterite nodule (d,e); Point 3: Chrompicotite piece (g,h).

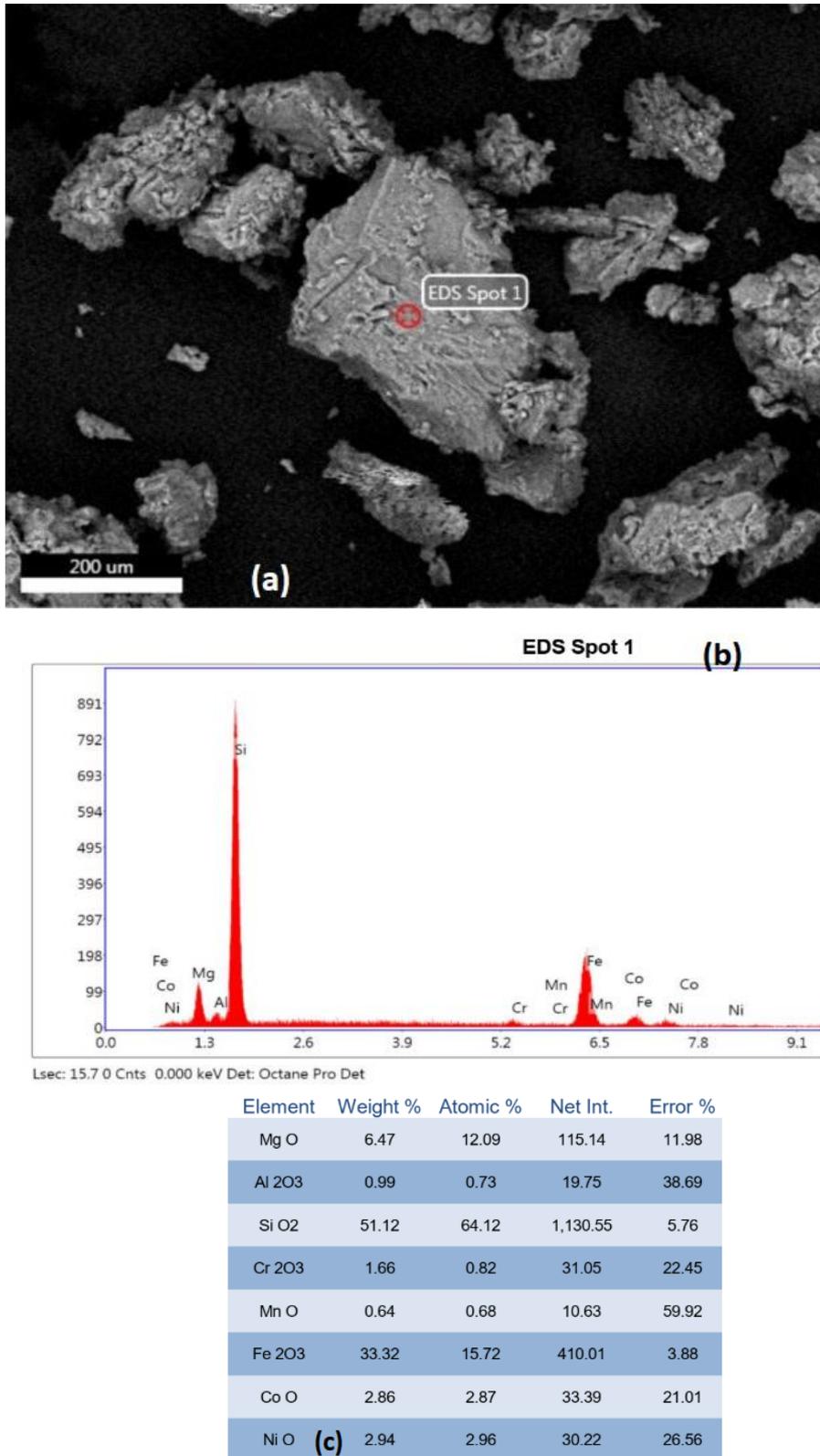


Figure 6. SEM/EDS analysis results of the samples from weakly weathered ultramafic rocks at outcrop 11 in Bai Ang area. SEM image of sample NN 11.1 (a): Weakly weathered rocks in the cross section at the pit wall of serpentine mine in Bai Ang area, The locations of EDS analysis points are marked in the image. The boxes below are the EDS plots of the shot points (left) and the results of the EDS analysis of that point (right). Point 1: ferisaponite clay (b,c); Point 3: Saponite/nontronite clay particles (d,e).

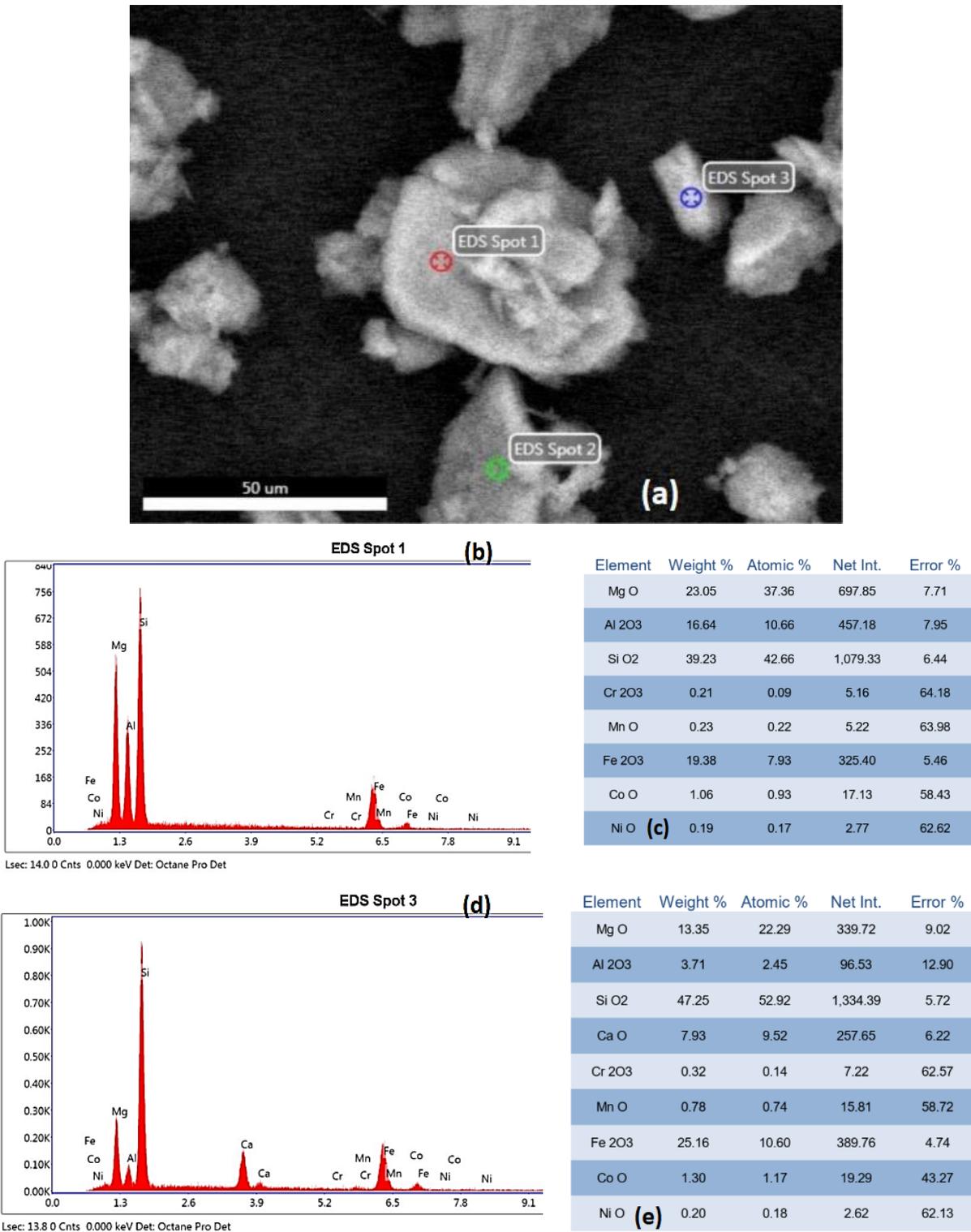


Figure 7. SEM/EDS analysis results of the samples from weakly weathered ultramafic rocks at outcrop 11 in Bai Ang area. SEM image of sample NN 11.1 (a): Weakly weathered rocks in the cross section at the pit wall of serpentine mine in Bai Ang area, The locations of EDS analysis points are marked in the image. The boxes below are the EDS plots of the shot points (left) and the results of the EDS analysis of that point (right). Point 1: ferisaponite clay (b,c); Point 3: Saponite/nontronite clay particles (d,e).

The analysis results of SEM/EDS samples showed that the Co and Ni content tended to increase significantly in the Fe-Mn spots/nodules. However, there is a difference between Ni and Co existence pattern: Ni tends to accompany Fe, while Co tends to be concentrated in Mn-rich sites. The analysis results also show that although Co is present in silicate minerals (hydrateserpentin, nontronite, saponite), its content is not as high as in Fe-Mn oxides/hydroxides.

The results of regolith geochemical research by Dao (1983) show that Ni-Co ore usually has a low content (Ni rarely exceeds 0.5%, Co has an average content of 0.03%). Although there are some samples with concentrations exceeding the general limit, in general, in the regolith as well as in the ultramafic bedrock, there is no Ni or Co ore body with an industrial scale.

In summary, in the weathering process of ultramafic rocks, when Ni is released from primary minerals, it will partly participate in the formation of secondary silicate minerals, partly in the lattice cell or adsorbed by Fe hydroxide (goethite) while Co ions will be highly adsorbed in the colloids (hydroxide) of Mn. This rule can also be applied when analyzing the formation process of Co accumulations in regolith/sediments in the Nui Nua area. Initial research results show that during the weathering of ultramafic rocks of Nui Nua massif, Co and Ni are released from primary minerals (serpentine, magnetite, chromite, etc.). The content of Co does not increase much in the weathering profile because the Co ion after being released is almost not participated in the structure of the secondary silicates but adsorbed in the colloids, due to the high affinity for Mn, it will be preferred to be adsorption in the Mn colloids (the precursors of asbolan and psilomelan) than in the colloids of iron (goethite, limonite). The results of the analysis of Co content in samples in the Nui Nua area and correlation with Mn content are completely consistent with this rule.

Although up to now, significant occurrences of Co (and also Ni) have not been found in bedrock and regolith in Nui Nua ultramafic massif. However, this is the source material for the valuable Ni and Co accumulations in Quaternary sedimentary materials around the Nui Nua area.

The potential of Ni and Co in the regolith as well as in the sedimentary materials around the Nui Nua block has been confirmed by a number of works. According to Decision No. 33/2007/QĐ-BCN dated July 26, 2007 of the Ministry of Industry: Approving the planning on zoning for exploration, exploitation, processing and use of chromite and manganese ores in the 2007-2015 period, towards the year of 2025, in the three mines Bai Ang, Mau Lam and Co Dinh, there are 3,076.87 thousand tons of Ni and 283.08 thousand tons of Co along with 20,972.94 tons of chromite.

Giang and Dung (2020), within the framework of the project "Research on technology to recover metal cobalt and nickel from waste sludge of chromite placere ore process Co Dinh, Thanh Hoa, Code: TEL.QG.CNKK.015/21" also said that the potential of Ni and Co in the bedrock and the regolith is very significant, but it requires more investment in research and appropriate technology to exploit. The authors have identified very interesting Ni and Co potentials in the waste sludge in the Mau Lam area. That result is a premise for further studies to clarify the prospect of Ni-Co in these sediments.

## 5. Conclusion

The analytical results show that the mineralogical composition of the regolith on the Nui Nua ultramafic rocks is mainly silicates belonging to the hydroserpentine group (hydrolizardite/chrysotile), smectite clay (nontronite, saponite, little montmorillonite) while the Fe-Mn hydroxides (Goethite/hydrogoethite asbolan/ psilomelan) contribute a significant part in the weathering profile. There are also minor minerals such as silicon oxide groups (quartz/chalcedony, opal), magnetite, chromite, and some other minerals.

During the weathering of Nui Nua ultramafic rocks, the Co content in the weathered crust increased, but not high. The SEM/EDS results indicate that cobalt and Ni concentrations are quite high in some specific minerals in the regolith of Nui Nua massif: the cobalt content in clay minerals (nontronite, saponite) fluctuates from 1÷2%, and especially high in Fe-Mn hydroxides (goethit and asbolan) with maximum value reached to 4.67%.

Although Cobalt occurred with low content in the weathering crust of Nui Nua Massif, this is a main source of industrial-level occurrences of Cobalt ore in the sediments around Nui Nua.

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### Contribution of authors

Thanh Trung Nguyen, Giang Khac Nguyen, Trong Huu Nguyen, Hai Manh Nguyen - field investigation at Nui Nua and collect samples; Thanh Trung Nguyen, Hai Manh Nguyen - collecting information related to Co and Ni and drafting the article; Thanh Trung Nguyen, Trong Huu Nguyen - sample processing and analysis; Giang Khac Nguyen, Chinh Cong Thi Vo - data processing and paper editing.

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