

Distribution and Mobility of Platinum-Group Elements in the Late Cretaceous Ni-laterite in the Northern Oman Mountains

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Abstract

Low-grade Ni-laterite deposits are well-developed over the mafic/ultramafic protoliths in the northern Oman Mountains. Concentrations, distribution patterns and mobility of platinum-group element (PGE) are investigated in some Ni-laterite profiles of the Oman ophiolite as a possible unconventional PGE resource. The ultramafic protolith displays the lowest PGE content (average total PGE = 35 ppb), which is almost similar to the PGE content in the overlying saprolite zone. The PGE content substantially increased upward in the laterite profile, where the highest total PGE content (up to 253 ppb) is recorded in the oxide and ferricrete/clay-rich zones. The highest PGE content corresponds to Pt > Ru > Pd, while the lowest PGE content is mostly corresponding to Os < Rh < Ir. There is a general positive correlation between PGE contents and both Cr₂O₃ and Fe₂O₃ contents in the Ni-laterite profiles. This may reflect the formation of PGE-Fe nanoparticle alloys that are hosted by Fe-rich oxyhydroxides or due to the residual accumulation of chromite in the oxide and ferricrete/clay-rich zones during the lateritization process. The PGE distribution patterns and positive correlation with the ultramafic index of alteration (UMIA) indicate that PGE can be mobilized in different proportions in the surficial environment upon progressive lateritization processes. The high concentration of total PGE in the Oman Ni-laterite is in good agreement with

the PGE-rich laterite deposits worldwide, which can be considered as an unconventional PGE resource if adequate extraction and refining processes can be applied for their recovery from the possible upcoming Ni production.

Keywords: Ni-laterite, platinum-group elements (PGE), ultramafic index of alteration (UMIA), Oman ophiolite

1. Introduction

Platinum-group elements (PGE) are considered among the so-called critical metals which are essential for the high technological industry. However, the conventional PGE deposits (e.g., stratiform chromitite and magmatic sulfide deposits) from which these metals can be extracted are very limited in the world. The oxidation and supergene enrichment process, also known as the lateritization process, is chemical weathering resulting in the dissolution, transportation, and redistribution of various elements at or near the Earth's surface. Laterite profiles produced by pervasive chemical weathering of mafic/ultramafic rocks were known to be an important source of metallic deposits such as nickel (Ni), cobalt (Co), and iron (Fe), which are known in literature as Ni-laterites (Evans, 1993; Freyssinet et al., 2005; Golightly, 2010; Thorne et al., 2012a, 2012b; Butt & Cluzel, 2013; Reich & Vasconcelos, 2015). Supergene enrichment process is also one of the important processes for residual and secondary enrichment of PGE and gold in these mineral deposits (Bowles et al., 1994; Gray et al., 1996; Varajão et al., 2000; Traoré et al., 2008; Aiglsperger et al., 2015, 2016, 2017; Rivera et al., 2018; Tobón et al., 2020). There is a consensus that three main processes are possibly controlling the PGE concentration and distribution in terrestrial rocks. They are partial melting, crystal fractionation, and post-magmatic alteration (Barnes et al., 1985). Platinum (Pt) and gold (Au) are more mobile than the other PGE during the weathering processes, while palladium (Pd) might be mobilized by hydrothermal fluids (e.g., Keays et al., 1981, 1982; Barnes et al., 1985; Stumpfl, 1986). Some Ni-laterite deposits show unexpectedly high total PGE contents (~ 4 ppm) such as those in the Acoje (Philippines) and Musongati and Kapalagulu (Burundi) laterites (Bandyayera, 1997), which can be used as unconventional PGE resource. These may add values to the lateritization processes as a potential agent for PGE accumulation via chemical weathering of mafic/ultramafic rocks. Despite that, the effect of lateritization on PGE enrichment and platinum-group minerals (PGM) accumulation is

still a matter of debate. In some places, PGE-rich (about 3 ppm) with accumulation of various types of PGM have been previously reported from Ni-laterites in the Falcondo laterite deposit of the Dominican Republic, which might be attributed to the presence of small chromitite pods associated with serpentized dunite (Proenza et al., 2007; Zaccarini et al., 2009; Proenza et al., 2010; Aiglsperger et al., 2015). Although the Ir-subgroup (IPGE = Os, Ir, and Ru) is considered to be highly resistant compared to the Pd-subgroup (PPGE = Rh, Pt, and Pd) under surficial conditions, several authors recognized that IPGE can also be mobilized under hydrothermal and/or lateritic weathering conditions (Stockman & Hlava, 1984; Garuti & Zaccarini, 1999; Zaccarini et al., 2005; Garuti et al., 2007, 2012). The lateritization process occasionally produces secondary PGE alloys, sulfides, sulfarsenides, and/or oxides/hydroxides by alteration of primary magmatic PGM precursors (Cornelius et al., 2008; Ndjigui & Bilong, 2010). However, supergene formation of PGM without the presence of magmatic PGM precursors has previously been reported from the platiniferous Au-Pd belt of Minas Gerais of Brazil (e.g. Cabral et al., 2009, 2011).

The Oman ophiolite represents one of the best-preserved oceanic lithospheres in the world, where a complete sequence of ophiolite stratigraphy is well-preserved and exposed from the upper mantle to the upper crust. The mantle sequence of the Oman ophiolite is essentially composed of tectonized harzburgite with minor dunites, lherzolites, and chromitites (Roberts, 1986). The mineralogical classification and general chemical characteristics of some Ni-laterite profiles from the northern mountains of the Oman ophiolite were previously studied to characterize the mineralization zones and their economic importance (Al-Khirbash, 2015, 2016, 2020; Al-Khirbash et al., 2014). The chromitite deposits of the Oman ophiolite were found to contain high content of PGE (Ahmed & Arai, 2002) and various types of PGM, which mainly comprised IPGE sulfides and, to a lesser extent, sulfarsenides (Ahmed & Arai, 2003). Oxidation of primary PGM sulfides into oxides is also described at low temperature conditions in the Oman ophiolitic chromitites (Ahmed et al., 2002). Desulfurization/oxidation is the main process in the surface environment that is responsible for the transformation of primary PGE sulfides into oxides and PGE-Fe alloys. To constrain the PGE distribution patterns, mobility, and concentration in supergene environments, their distribution in the Ni-laterite of the Oman ophiolite is analyzed in the present research. In this contribution, a detailed bulk-rock analysis and PGE geochemistry from six different Ni-laterite profiles of the Northern Oman Mountains is thoroughly studied with the aim

to understand the behavior, distribution, and mobility of PGE in the oxidation and supergene environments. A comparison with world-class laterite deposits is also done to assess the economic potentiality of the PGE in the Oman Ni-laterites.

2. Geologic settings

The present study is located at about 180 km SW of Muscat and lies around Saqah town between N 22° 45` and 22° 50` and 58° 40` 58° 50` (Figure 1a). The area is covered by the Late Cretaceous allochthonous ultramafic/mafic rocks of the Semail ophiolite nappe that was emplaced as a result of the obduction of the Tethyan rocks onto Middle Permian to Middle Cretaceous shelf carbonate sequences of the Arabian passive continental margin (Glennie et al., 1974; Coleman, 1981; Boudier et al., 1985; Dercourt et al., 1986; Lippard et al., 1986; Skelton et al., 1990; Searle & Cox, 2002; Peters et al., 2005; Searle, 2019). Small outcrops exposed on the eastern part of the study area consist of the deep marine limestone, radiolarian chert, and pelagic sediments (Hawasina window) and low-grade epidote greenschist facies metasedimentary rocks, cherts, marbles, and quartzites (metamorphic sole) (Cowan et al., 2014) (Figure 1b).

The Ni-laterites from the Northern Oman Mountains are part of the Maastrichtian neo-autochthonous post-obduction terrigenous clastic facies (Qahlah Formation) and lie unconformably on the obducted Semail ophiolite while they are capped by post-obduction Late Campanian/Maastrichtian–Tertiary sedimentary rocks of the Simsim formation (Abbasi et al., 2014). The presence or absence of the laterite in the Northern Oman Mountains might reflect the original irregular paleotopography, the existence of basins associated with syn-sedimentary structures, and the prevailing climatic conditions at the end of the Cretaceous period that all initiated an intense and prolonged weathering process of the ophiolite (Nahon et al., 1982; Nolan et al., 1990; Al-Khirbash et al., 2010).

This work is based on field work and mineralogical and physical characteristics of laterite from six localities (1 to 6) in the Northern Oman Mountains (Figure 1). Localities 3 and 4 were combined in one profile as they logged along two sides of the road cut. The studied laterite profiles can be grouped into two main zones: the protolith zone and the laterite zone (Figure 2). The protolith consists of either relatively unweathered layered gabbro or serpentinized peridotite in the

most localities (Figures 2, 3a, 3b). The laterite zone comprises the in-situ green to grayish saprolite horizon, the reddish to brown massive to pisolitic oxide horizon, and the upper ferricrite or in some localities the compact clay-rich horizon (Figures 2, 3c, d, e, f).

The presence of protolith relics within the saprolite zone, gradual changes of element distribution (from the protolith to the upper zones), and the survival of chromian spinel and Cr-rich magnetite within the laterite zones, all reflect in-situ development of laterite materials in the northern Oman Mountains. A detailed field and mineralogical description of these zones was given by Al-Khribash (2015, 2016).

3. Sampling and analytical techniques

Twenty-nine samples were collected from six lateritic profiles in the Oman Mountains (six from the protolith, 4 from the saprolite zone, 15 from the oxide zone, 4 from the clay/ferricrite zone) for PGE and Au analyses (Figure 2). Samples were selected based on the mineralogical and geochemical characteristics of previous studies (Al-Khribash, 2015, 2016), particularly those that showed high content of Cr-Ni-Co. The rock samples were broken into small chips using a hydraulic rock splitter and then pulverized using a Fritsch Pulverisette 5 planetary mill for 30 to 45 minutes. Samples up to 60 g in size were assayed using a nickel sulfide (NiS) fire assay Neutron Activation Analysis (INAA) procedure. The nickel sulfide was dissolved in concentrated HCl, and the resulting residue, which contains all the PGE and Au, was collected on a filter paper. The residue underwent two irradiations and three separate counts to measure all the PGE and Au. One batch of analyses consists of the 29 samples in addition to two blanks, three certified standards, and three duplicates. Detection limits were as follows: Os (2 ppb), Ir (0.1 ppb), Ru (5 ppb), Rh (0.2 ppb), Pt (0.5 ppb), Pd (2 ppb), and Au (0.5 ppb). All analyses were carried out at Activation Laboratories Ltd. (Ancaster, Ontario, Canada).

Thin sections were prepared and subsequently investigated under transmitted optical microscopy. Selected samples from different laterite zones were examined with a PANalytical X'Pert PRO X-ray diffractometer with Cu λ K α =1.54060 Å, a Ni Filter at 40 kV and 45 mA. The XRD patterns were recorded at a time step of 0.4 s for 2θ varies from 5° to 70°. The XRD analyses

were carried out at the Central Analytical and Applied Research Unit (CAARU) Sultan Qaboos University (Oman).

4. Petrography

Microscopic studies of the protoliths showed that the layered gabbro consists of fresh to altered plagioclase crystals with some altered pyroxenes (Figure 4a), and the serpentinized peridotites consist of pyroxene crystals that are altered to lizardite and chrysotile (Figure 4b). The above saprolite horizon comprises compact gray-greenish color rocks with abundant light-green lizardite and chrysotile minerals and commonly contains carbonate-filled fractures (Figure 4c). The oxide horizon is predominantly composed of hematite and goethite with rounded and ellipsoidal pisolite appearance (Figure 4d). The upper ferricrete/ironstone horizon consists mainly of massive hematite, goethite with magnetite, and inherited chromite grains that are replaced by hematite and authigenic chlorite (Figures 4d, e). XRD data confirmed the presence of these minerals (Figure 5).

5. Geochemistry

5.1 Major and compatible trace element geochemistry

Based on mineralogical characteristics as well as variations in physical properties such as texture, structure, and color, the laterite profiles of the Oman ophiolite can be classified into four categories: (1) protolith, which is represented by serpentinized peridotites and layered gabbros; (2) saprolite, which is the partly weathered zone overlying the protolith; (3) oxide zone, and (4) the ferricrete/clayrich zone, which represents the uppermost part of the laterite profiles. Geochemically, there are slight differences in major and compatible trace elements contents between the protolith and saprolite zones. Thus, they will deal together in the following descriptions, however they are clearly discriminated in figures and tables. On the other hand, the oxide and ferricrete/clayrich zones show significant geochemical differences compared with the protolith and saprolite zones. The major and selected compatible trace (Cr, Ni, Co) elements compositions of the protolith, saprolite, and oxide, and ferricrete/clayrich zones of the studied laterite profiles are shown in Tables 1 and 2.

5.1.1 Protolith and saprolite zones

The Ni-laterite profiles of the Oman Mountains are well-developed over serpentinized peridotites and/or over layered gabbros (Figure 2). The serpentinization process of ultramafic rocks adds water into the system, where serpentinized peridotites can contain more than 13 wt.% of water in the produced hydrous mineral crystal structure (e.g., Deschamps et al., 2013). However, a careful description of the samples should be done because the loss on ignition (LOI) is not always correlated with the degree of serpentinization since the presence of other hydrous phases such as talc, brucite, chlorite, and clay minerals can influence this budget. Careful petrographic investigation and X-ray diffraction (XRD) analysis of the studied serpentinized peridotite protolith of the Oman laterite profiles confirm the absence of such hydrous minerals, except the lizardite, antigorite, and clinochrysotile that represent the major mineral phases in the studied serpentinized peridotite protolith (Figure 5) (Al-Khirbash, 2016). The peridotite protolith of all laterite profiles shows the same compositional ranges in terms of their LOI and major and compatible trace elements constituents. The LOI of the peridotite protolith varies from 14.72 wt.% to 16.18 wt.%, with an average of 15.43 wt.% (Table 1). The low CaO content (0.05–2.82 wt.%, with an average of 0.97 wt.%) in the serpentinized peridotites reveals that serpentinization is the only process affecting the peridotite protolith. The LOI in the saprolite zone shows comparable values to the underlying serpentinized peridotites, varying from 14.59 wt.% to 15.88 wt.%, with an average of 15.27 wt.%, and a similar range of CaO content (Table 1). The common major oxides (SiO_2 , MgO , Fe_2O_3 , and Al_2O_3) do not show significant differences between the peridotite protolith and the overlying saprolite zone, where the average contents of these components are 37.23 wt.%, 36.08 wt.%, 7.78 wt.%, and 1.16 wt.%, respectively, in the former and 38.32 wt.%, 35.17 wt.%, 8.23 wt.%, and 0.79 wt.%, respectively, in the latter (Table 1). The most compatible trace elements (e.g., Cr_2O_3 , NiO , Co_3O_4 , and MnO) show comparable values in both the saprolite zone and the underlying peridotite protolith. The average NiO content in the saprolite zone (0.26 wt.%) is relatively higher than those in the underlying peridotite protolith (0.18 wt.%) (Table 1). The Cr_2O_3 and MnO contents are almost similar in the peridotite protolith and in the saprolite zone. They are averaging 0.38 wt.%, 0.36 wt.%, and 0.13, 0.11 wt.%, respectively (Table 1).

5.1.2 Oxide and ferricrete/clayrich zones

The upper oxide and ferricrete/clay-rich zones of the laterite profiles show significant differences in terms of the LOI, major constituents, and compatible trace elements compared with their protolith and saprolite zones. In terms of the major constituents, the distinguishing feature of these uppermost parts of the laterite profiles is the substantial increase in Fe_2O_3 and Al_2O_3 contents and the extreme leaching of SiO_2 and MgO compared with the underlying protolith and saprolite zones. The oxide and ferricrete/clayrich zones of the studied laterite profiles show comparable data of wide compositional ranges in terms of their major and compatible trace element constituents. SiO_2 is the most prominent component that is progressively decreased from the protolith to the uppermost oxide and ferricrete/clayrich zones. It displays reverse correlation with both total iron, as Fe_2O_3 , and Al_2O_3 contents (Figures 6a, b). The SiO_2 content varies from 27.06 wt.% in the less lateritized samples down to 2.23 wt.% in the strongly lateritized ones (Table 2). The total iron, as Fe_2O_3 , is highly increased with the increasing degree of lateritization. It varies from 31.14 to 85.50 wt.% and from 16.82 to 78.18 wt.% in the oxide and ferricrete/clay-rich zones, respectively (Figure 6a). The Al_2O_3 content shows the highest value in the ferricrete/clay-rich zone, where it reaches up to 24.49 wt.%, and the lowest Al_2O_3 value (1.70 wt.%) is reported in the oxide zone (Figure 6b). MgO , on the other hand, is the most leachable component in the oxide and ferricrete/clay-rich zones of the laterite profiles. It is decreased to 0.40 and 0.37 wt.% in the highly lateritized samples of the oxide and ferricrete/clay-rich zones, respectively (Figures 6c, d). The MgO content shows strong positive and negative correlations, respectively, with SiO_2 (Figure 6c) and Fe_2O_3 (Figure 6d). In terms of the compatible trace elements (Cr, Ni, Co, and Mn), they are highly (Cr and Ni) to slightly (Co and Mn) enriched in the oxide and ferricrete/clay-rich zones of the laterite profiles compared with the protolith and saprolite zones (Table 2). Cr_2O_3 is the most enriched compatible component in the uppermost oxide and ferricrete/clay-rich zone, where it reaches up to 5.35 wt.% (3.36 wt.% average) and 11.44 wt.% (5.47 wt.% average) in the two laterite zones, respectively (Table 2). Similarly, the NiO content in the oxide and ferricrete/clay-rich zones of the laterite profiles reaches up to 2.85 wt.% (1.11 wt.% average) in oxide zone, and up to 2.01 wt.% (0.70 wt.% average) in the ferricrete/clay-rich zone. It is highly enriched in the oxide zone (up to 11 times greater than the Ni content in the protolith) and in the ferricrete/clay-rich zone (up to 8 times greater than the Ni content in the protolith). NiO content is generally increased with increasing Fe_2O_3 and Al_2O_3 contents (Table 2 and Figure 7a). The Co_3O_4 and MnO contents also relatively increase in the oxide and ferricrete/clay-rich zones, which reach up to 0.50 wt.% and 2.52 wt.%,

respectively (0.11 wt.% and 0.36 wt.% on average), showing a good positive correlation with NiO and Fe₂O₃ contents (Table 2).

5.2 Platinum-group elements (PGE) geochemistry

5.2.1 Protolith and saprolite zones

The PGE contents in the serpentinized peridotite and the saprolite zones in all profiles are similar, with very limited variations (Table 1). The total PGE content of the serpentinized peridotite protolith ranges between 20 and 36 ppb (31 ppb on average), which shows approximately flat chondrite-normalized PGE distribution patterns (Figure 9a) with slight positive fractionation ratios (average Pd/Ir_N and Ru/Pt_N = 1.54 and 0.99, respectively). It is noteworthy that the total IPGE (= Os, Ir, and Ru) is progressively increased along with the increase of PPGE (= Rh, Pt, and Pd) from the protolith to the saprolite and then to the oxide and ferricrete/clay-rich zones of the laterite profiles (Figure 8). The saprolite samples of laterite profiles show relative enrichment in total PGE compared with the serpentinized peridotites, varying from 36 to 93 ppb (58 ppb on average), which is mostly showing flat PGE distribution patterns, but sometimes with pronounced positive trend from Os to Ru then flat from Rh to Pd (Table 1 and Figure 9b). The Pd/Ir_N and Ru/Pt_N fractionation ratios reflect the relative enrichment in the IPGE compared with the PPGE. The average Pd/Ir_N and Ru/Pt_N ratios in the saprolite samples are 1.93 and 1.43, respectively. The Au content in the peridotite protolith and saprolite zones is approximately similar, which varies from 1 upto 5 ppb (Table 1).

5.2.2 Oxide and ferricrete/clay-rich zones

The total PGE content in the oxide and ferricrete/clay-rich zones of the laterite profiles is very high compared with those in the protolith and saprolite zones. The enrichment factor reaches up to six times in the oxide and ferricrete/clay-rich zones. Total PGE content varies from 59 up to 253 ppb (139 ppb on average) in the oxide zone, and from 43 to 176 ppb (107 ppb on average) in the ferricrete/clay-rich zone (Table 2). Both IPGE and PPGE sub-groups are substantially increased in the oxide and ferricrete/clay-rich zone of the laterite profiles, showing a general positive trend from Os to Pd in the chondrite-normalized PGE distribution patterns (Figures 9c, d). There is an obvious enrichment in the total PGE contents, with promotion of the lateritization process from the protolith upward to the uppermost oxide and ferricrete/clay-rich zones, which is reflected by

the substantial increase in Fe₂O₃, Cr₂O₃, and NiO contents (Figures 7b–d). The Pd/Ir_N and Ru/Pt_N ratios also reflect the general increase in both IPGE and PPGE in the PGE distribution patterns, which vary respectively from 0.45 to 3.81 (1.43 on average) and from 0.51 to 7.75 (2.78 on average) in the oxide and ferricrete/clay-rich zones. The Σ IPGE/ Σ PPGE ratio varies from 0.3 to 0.86 (0.61 on average) in the peridotite protolith, from 0.52 to 2.11 (1.12 on average) in the saprolite, and from 0.31 to 2.18 (1.16 on average) in the oxide/ ferricrete/clay-rich zone. There is a clear progressive increase of both IPGE and PPGE contents upward from the protolith to the oxidized zone of the laterite profiles (Figure 8). The Au content in the oxide and ferricrete/clay-rich zones is relatively higher than those in the protolith and saprolite zones. It reaches up to 15 ppb in the ferricrete/clay-rich zone (Table 2).

6. Discussion

6.1 Degree of lateritization

When the mafic/ultramafic rocks are exposed to the surface, they undergo intense chemical and mechanical weathering processes, which are mainly controlled by climatic and topographic conditions (Golightly, 1981, 2010; Freyssinet et al., 2005). These oxidation and supergene processes lead to the leaching of major elements (i.e., MgO and SiO₂) from the ferromagnesian minerals (olivine and pyroxenes) in parent rocks, whereas other elements (e.g., Ni, Mn, and Co) can be enriched up to ~~the~~ economic values (Aiglsperger et al., 2016). Water-insoluble oxides ~~metals~~ such as Fe₂O₃, Al₂O₃, and Cr₂O₃ are also residually accumulated in situ as oxides and oxyhydroxides, which play an important role as metals-retention phases in the uppermost part of the laterite profiles (Butt & Cluzel, 2013; Bowles et al., 2017). To evaluate the degree of lateritization and chemical changes in ultramafic rocks during the formation of Ni-laterite, Aiglsperger et al. (2016) defined a factor called ultramafic index of alteration (UMIA), which is mainly based on the index of lateritization (IOL) proposed by Babechuk et al. (2014). The UMIA is calculated using the molar ratios of the major element oxides from the wt.% contents of the whole rock analysis (Duzgoren-Aydin et al., 2002), and the IOL is calculated as the wt.% of the major oxides (Babechuk et al., 2014; Aiglsperger et al., 2016; Tupaz et al., 2020). The following equations are used to calculate the UMIA and IOL:

$$\text{UMIA} = 100 \times [(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_{3(\text{T})})/(\text{SiO}_2 + \text{MgO} + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_{3(\text{T})})]$$

$$\text{IOL} = 100 \times [(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_{3(\text{T})})/(\text{SiO}_2 + \text{MgO} + \text{Fe}_2\text{O}_{3(\text{T})})]$$

These weathering indexes depend on the composition of ultramafic rocks (i.e., peridotites) that are essentially dominated by MgO and SiO₂, with negligible amounts of CaO, Na₂O, and K₂O (Babechuk et al., 2014). The breakdown of primary minerals is occasionally followed by the development of secondary minerals such as serpentine, chlorite, clay minerals, and oxyhydroxide phases (e.g., Fe-Mn oxides and hydroxides) (Rivera et al., 2018). Thus, the values of UMIA and IOL indexes give important information about the weathering trend of ultramafic rocks, which can also be shown as ternary diagrams of A-SM-F [(Al₂O₃-(SiO₂+MgO)-Fe₂O₃)] and AF-S-M [(Al₂O₃+Fe₂O₃)-SiO₂-MgO] (Figures 10a, b), and the IOL is shown as ternary S-A-F (SiO₂-Al₂O₃-Fe₂O₃) ternary diagram (Figure 10c). The UMIA of the ultramafic protolith of the Oman Ni-laterite ranges from 3% to 5%, with an average of 4%, and the less weathered saprolite samples are more or less similar to the underlying protolith where the values of UMIA vary from 3% to 4% (Figure 10a). The oxide and ferricrete/clay-rich zones of the laterite profiles have UMIA values between 38% and 88% (69% on average) in the oxide zone, and from 39 – 89% (73% on average) in the ferricrete/clay-rich zone (Table 2, Figures 10a, b). The IOL, on the other hand, is comparable with the UMIA values, where the average values in the protolith, saprolite, oxide and ferricrete/clay-rich zones are 4%, 4%, 78% and 84%, respectively (Figures 10a–c). Except one sample from locality #1 where the Al₂O₃ content is exceptionally high, the Ni-laterite profiles of the Oman ophiolite are characterized by constantly high Fe/Al ratios (Figures 10a–c and Table 2). It is obvious that both Al₂O₃ and Fe₂O₃ contents are progressively increased with the increasing degree of lateritization (i.e., UMIA) toward the surface of the laterite profiles. There is a good direct relationship between the two components, from the ultramafic protolith to the oxide and ferricrete/clay-rich zones (Figure 11a). The Ni and Co, which are mainly hosted by ferromagnesian minerals (e.g., olivine and pyroxenes) in the parent rocks, are also progressively increased with the increasing degree of lateritization (Figure 11b), as concluded by Al-Khirbash (2016), and are hosted by goethite, chlorite, kaolinite, and other Ni-bearing serpentine and talc (Al-Khirbash 2015). The residual accumulation of chromite in the uppermost part of laterite profiles is also obvious, which clearly increases with the increasing process of lateritization (Figure 11c). This is also clearly shown by the enrichment of total PGE with the increase in Cr₂O₃ contents in the laterite profiles. This is because chromite is considered as one of the main hosts of PGE in general and IPGE in particular (Table 2). Based on the calculated UMIA and IOL values, the Oman Ni-

laterite are in a good agreement with the moderately lateritized profiles worldwide (Babechuk et al., 2014; Rivera et al., 2018).

6.2 PGE enrichment in Ni-laterite

In general, the total PGE contents in Ni-laterites around the world are ranging between ≤ 100 ppb and up to few hundreds ppb in content (Augé & Legendre, 1994; Eliopoulos & Economou-Eliopoulos, 2000; Ndjigui & Bilong, 2010; Aiglsperger et al., 2015, 2016; Rivera et al., 2018). However, in some places, exceptionally enriched lateritic crusts with 2 ppm, as well as more than 4 ppm total PGE, were reported in the Ora Banda Sill in Western Australia (Gray et al., 1996) and in Burundi (Maier et al., 2008). In all of the studied Ni-laterite profiles from the Northern Oman Mountains, the uppermost oxide and ferricrete/clay-rich zones show the highest PGE contents compared with the saprolitic zone and the underlying protolith. The anomalous concentration of PGE contents in the upper levels of the weathering profile, compared with their initial low contents in the underlying bedrocks, as well as the positive correlation between the UMIA and total PGE contents (Figure 11d), indicate that PGE can be mobilized in different proportions throughout the weathering profile (e.g., Aiglsperger et al., 2016; Rivera et al., 2018; Tobón et al., 2020). From the PGE distribution patterns (Figures 9a–d), it is clearly shown that Ru, Pt, and Pd are more mobile than Ir and Rh, while Os shows the highest mobility in the surficial environment where it is mostly leached out from the weathered profiles. The pronounced Ru positive anomalies from all of the studied laterite profiles are mostly attributed to its presence as laurite (RuS_2) crystals, or as Ru-Fe alloys, within the residually accumulated chromite grains in the weathered laterite profiles. Although PGM grains were not reported from the studied Ni-laterite profiles (it needs more careful observations under high magnifications), it is confirmed from previous studies on the Oman ophiolite where the main PGE mineralogy are laurite in the primary chromite (Ahmed & Arai, 2003) and PGE oxides in weathered lithologies (Ahmed et al., 2002). The residual accumulation of chromite grains (represented by high Cr_2O_3 content) in the oxide and ferricrete/clay-rich zones compared with the Cr_2O_3 content in the protolith and saprolite zones (Fig. 7c) (at least 10 to 15 times greater than the protolith content), can substantially contribute to the high Ru content. The PGE mobility in surficial environments can be attributed to the lateritization processes that resulted in the migration of these metals toward the oxide and oxyhydroxide zones (Eliopoulos & Economou-Eliopoulos, 2000; Talovina & Lazarenkov, 2001; Ndjigui & Bilong, 2010; Aiglsperger

et al., 2015). The PGE mobility and redistribution within the laterite profile are most probably controlling by: (1) the Eh–pH ratio of the weathering solutions, (2) the Cl concentration in the laterite profile, and (3) the mode of occurrence of PGM in the parent rocks before weathering (Bowles et al., 1994a, 1994b; Salpéteur et al., 1995; Ahmed & Arai, 2002, 2003; Ahmed et al., 2002). In addition to the Pt-Pd-Cl complexes, the Pt and Pd as redox metals can also be mobilized as inorganic complexes in low temperature conditions (Colombo et al., 2008). The highly accumulated chromite grains in the uppermost part of the weathered profiles of the Oman ophiolite (Figure 11c) could be accompanied by the enrichment of total PGE, in general, and IPGE, in particular. The IPGE, which have higher melting points than the PPGE, tend to be concentrated in refractory phases (i.e., chromite) and in early cumulates relative to PPGE, which are more incompatible and tend to be retained in the residual melt and crystallized with the interstitial sulfide phase (Barnes et al., 1988; Edwards, 1990; Prichard et al., 1996a, 1996b). Thus, PPGE could be easily mobilized and redistributed during the chemical weathering of parent rocks than the IPGE, which are mainly related to the chromite accumulation. The available data, however, suggests that Os is amongst the most soluble PGEs under the surficial conditions, where it shows the lowest content in all of the studied laterite profiles. Both mechanisms, the leaching of PPGE from the interstitial sulfide phase and the accumulation of IPGE with chromite, will lead to the increase in both of them in the oxide and ferricrete/clay-rich zones of the laterite profiles (Figure 8).

Previous studies on the mobility of PGE during lateritization processes revealed that acidic conditions ($\text{pH} < 6$ and $\text{Eh} > 0.4$) could lead to the dissolution of PGE-bearing minerals, especially PPGE phases, and then they would undergo subsequent transportation in solution and accumulation in the oxidized Fe-rich laterite profiles (Plimer & Williams, 1988; Bowles et al., 1994a, 1994b; Talovina & Lazarenkov, 2001). The PGE are accumulated as PGE-rich alloys, which co-precipitate with Fe and Mn oxides under such acidic conditions (Bowles et al., 1994a, 1994b; Salpéteur et al., 1995; Ndjigui & Bilong, 2010; Tobón et al., 2020). Complex Pt-Ir-Fe-Ni alloys were recently found as inclusions and packed nanoparticles within pore spaces of Fe oxides and oxyhydroxides of the Loma Peguera Ni-laterite deposit in the Dominican Republic (Aiglsperger et al., 2015, 2017) and in the Planeta Rica Ni-laterite profiles of Northern Colombia (Tobón et al., 2020). These observations are in good agreement with the previous studies, which indicated that the high contents of Pt, Pd, and Ru, as well as the transition metals such as Ni, Co, Cu, and Zn, in laterite profiles, are essentially hosted by secondary minerals like Fe-oxy-

hydroxides or smectite clay minerals (Oberthür & Melcher, 2005; Ndjigui & Bilong, 2010). The high total PGE contents in the oxide and ferricrete/clay-rich zones of the Oman Ni-laterite profiles are in accordance with this idea and could be accumulated as PGE-Fe alloys that co-precipitated with oxides and oxyhydroxides. The newly formed supergene PGE alloys could be formed in situ during lateritization processes by dissolving the primary magmatic PGM precursor (Aiglsperger et al., 2016).

6.3 Possible economic potentiality

Although the total PGE contents (< 300 ppb) in the Ni-laterite profiles of the Oman ophiolite do not reach the economic values, they are mostly comparable to the total PGE contents reported from PGE-rich Ni-laterite profiles around the world, such as Ni-laterite deposits of Falcondo in the Dominican Republic, Cuba (Aiglsperger et al., 2015, 2016), and New Caledonia (Traoré et al., 2008); Ni-laterite from Centinela Bajo, south-central Chile (Rivera et al., 2018); and those from the Cerro Matoso and Planeta Rica Ni-Laterite deposits, Northern Colombia (Tobón et al., 2020). For example, the Ni-laterite deposit of Falcondo of the Dominican Republic has PGE values before processing between 250 and 640 ppb. However, the final product obtained after pyrometallurgical extraction shows an increase in total PGE contents up to 2 ppm (Aiglsperger et al., 2015, 2016). Similarly, in the Ni-laterite deposits of Cuba, the PGMs are mainly collected in the sulfide concentrates and the Ni-end products during the ore dressing in the Nikaro and Moa ore dressing plants, where the PGE contents reach up to 6 ppm (Lazarenkov et al., 2005). Such final PGE values are considered as a potential unconventional PGE resource from the Falcondo and Cuba Ni-laterite deposits.

In the Ni-laterite profiles of the Oman ophiolite, the PGE contents in the oxide and ferricrete/clay-rich zones reached up to 253 ppb (up to 6 magnitude as those in the parent ultramafic rocks), which is almost comparable to those reported from worldwide PGE-rich Ni-laterite deposits (Figure 12). The PGE enrichment in the oxide zone of the laterite profiles corresponds to an increase in NiO, Co₃O₄, Cr₂O₃, Fe₂O₃, and Al₂O₃ contents, as well as to the highest calculated degrees of lateritization (average UMIA ~70%) (Figures 11a–d). The formation of secondary nanoparticles of PGE alloys in the oxide and oxyhydroxide zones of the Oman laterite profiles needs more careful investigation using ultrahigh magnification tools such as the field emission scanning electron microscope (FESEM) and/or Raman spectroscopy techniques, which is beyond the scope

of this article. In addition, further field investigations and systematic sampling are needed to focus on the profiles having more concentration of Cr_2O_3 contents and progressive high degrees of lateritization. Although the PGE contents in the oxidized horizons of the Oman Ni-laterite profiles are not economic in its current natural form, applying adequate extraction and refining methods in the future could increase the PGE contents, which might be recovered as by-products. If it is applied in the future, the Ni laterite of the Oman ophiolite can be considered as unconventional PGE deposits.

6. Conclusions

1. The Ni-laterite profiles of the Oman ophiolite characterized by the progressive increase in Fe_2O_3 , Al_2O_3 , Cr_2O_3 , NiO , and Co_3O_4 contents from parent ultramafic rocks to the oxide and ferricrete/clay-rich zones in the uppermost part of the laterite profile. This also corresponds to the strong leaching of SiO_2 and MgO contents from the oxidized zone of the laterite profiles.
2. The highest PGE contents in the Ni-laterite of the Oman ophiolite are concentrated in the oxide and ferricrete/clay-rich zones, which reached up to six times as their contents in the saprolite and peridotite protolith. The PGE distribution patterns and positive correlation of total PGE contents with the UMIA, as well as the increase of Cr_2O_3 contents in the oxide and ferricrete/clay-rich zones of laterite profiles, indicate that the PGE can be mobilized in different proportions.
3. Ru, Pt, and Pd are more mobile than Os, Ir, and Rh. The positive correlation between IPGE and PPGE with the increasing degree of lateritization is indicative of their mobilization, redistribution, and enrichment in the Fe-rich oxides and oxyhydroxides of the laterite profiles. The IPGE are most probably, at least partly, linked with the residual accumulation of chromite in the oxide and ferricrete/clay-rich zones, while the PPGE are most probably leached from the interstitial sulfides.
4. The PGE contents of the Oman Ni-laterite are in accordance with the PGE values from the worldwide Ni-laterite deposits. It can be considered as an unconventional PGE resource if adequate extraction and refining processes are applied to increase the PGE contents in the final products.
5. Further field investigations focusing on the Ni-laterite profiles with high degrees of lateritization and those enriched in Cr_2O_3 contents are needed to check the existence of PGE

enrichment in these laterite profiles. A detailed mineralogical study using ultrahigh magnification tools is also needed to identify the possible presence of PGE-Fe alloy nanoparticles in the oxide and oxyhydroxide zones of the Ni-laterites.

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The authors declare that there is no conflict of interest.

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Figure 6: Compositional binary variation diagrams of major oxides of the studied Ni-laterite of the Oman Mountains. a, b, and c are variations of SiO_2 vs. Fe_2O_3 , Fe_2O_3 , and MgO wt.%, and d is the variation of Fe_2O_3 vs. MgO wt.%.

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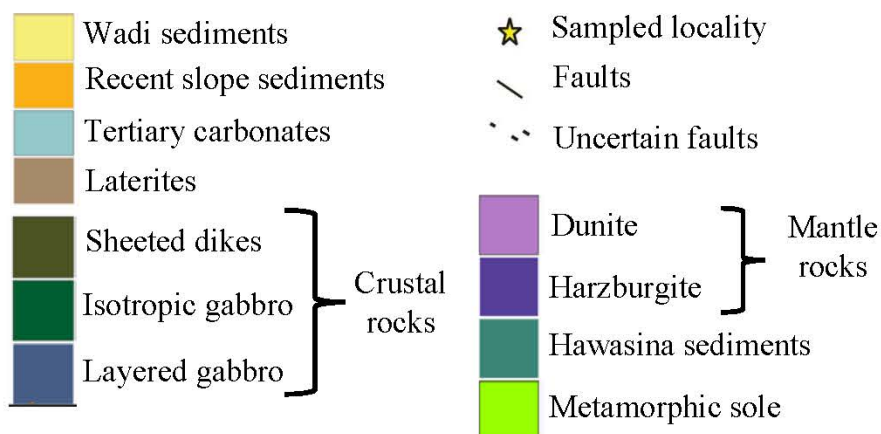
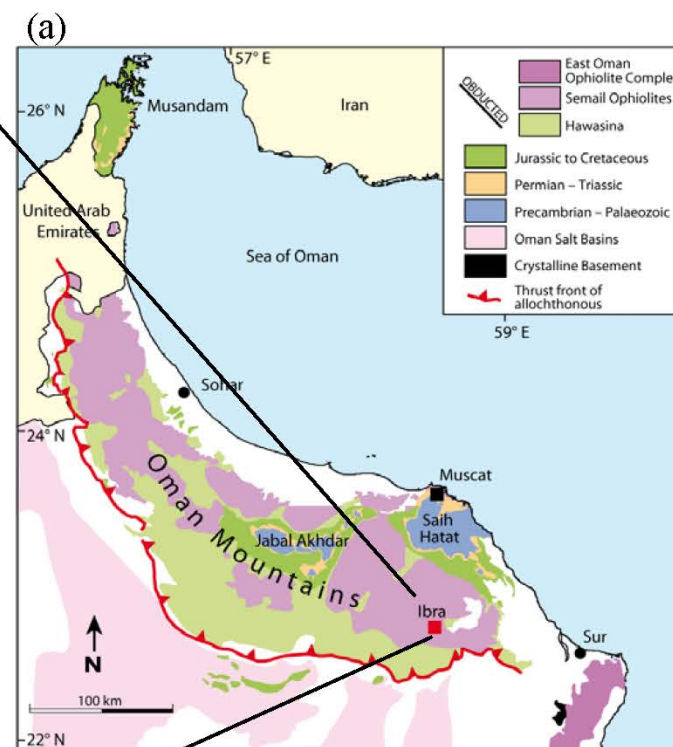
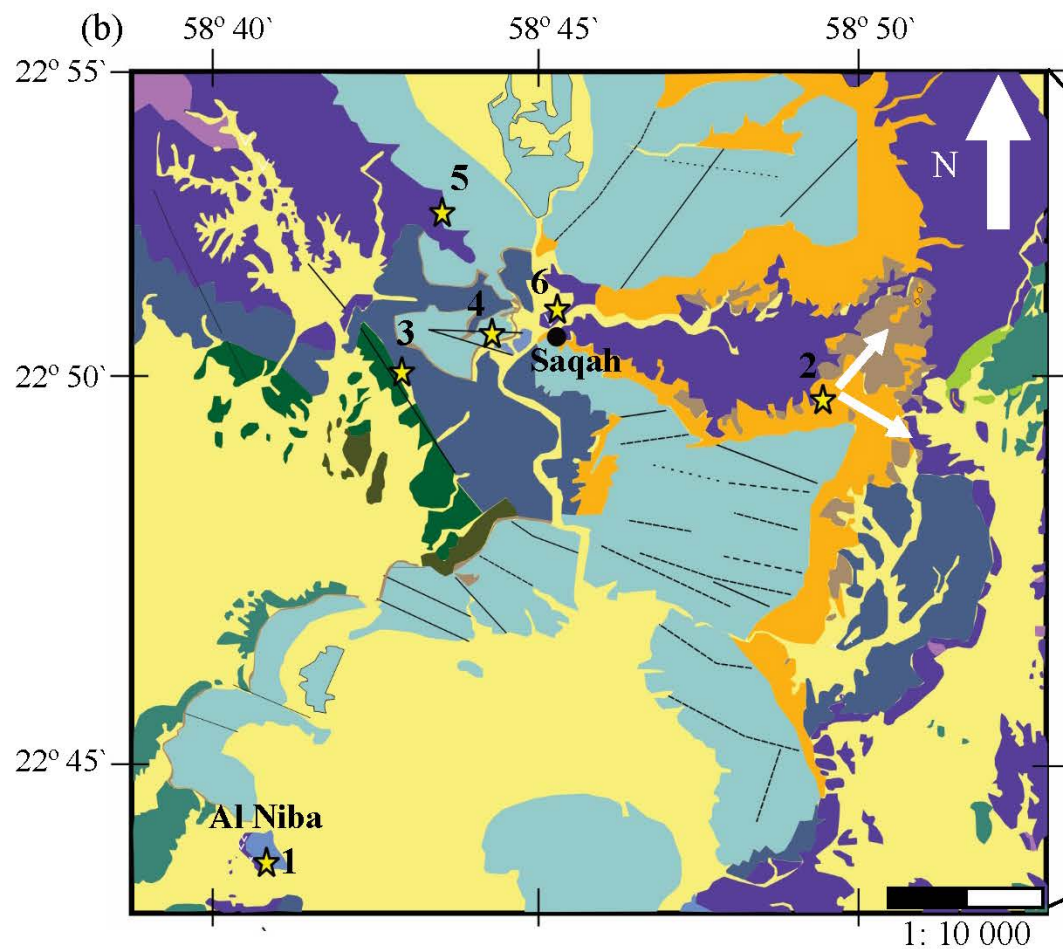
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Table 2: Major, selected trace elements composition (wt.%) and PGE contents of the oxide and ferricrete/clay-rich zone samples of the studied Ni-laterite profiles of the Oman ophiolite.



Locality #:

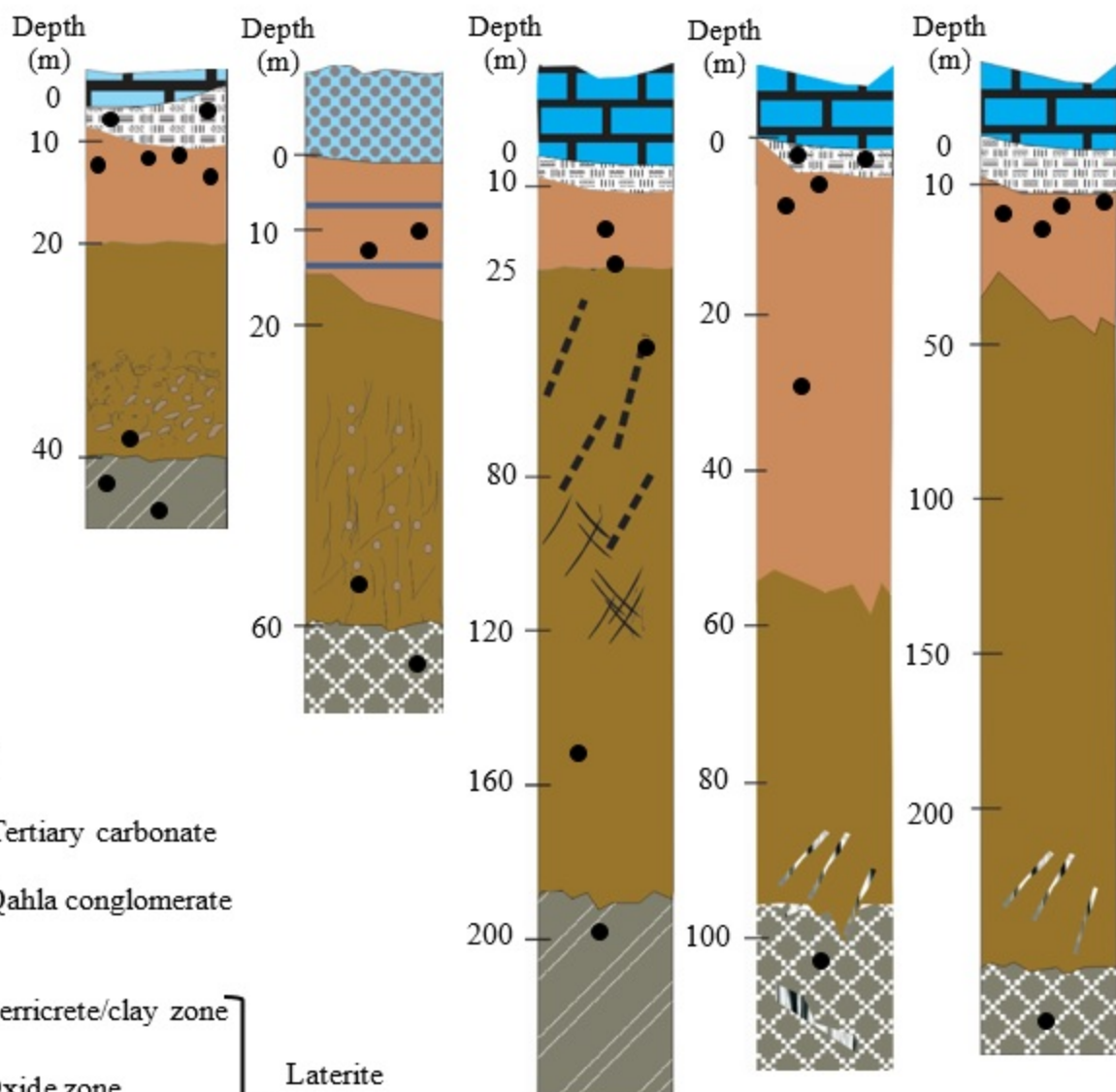
1

2

3 and 4

5

6



Legend



Tertiary carbonate



Qahla conglomerate



Ferricrete/clay zone



Oxide zone



Saprolite zone

} Laterite zones



Layered gabbros



Peridotites

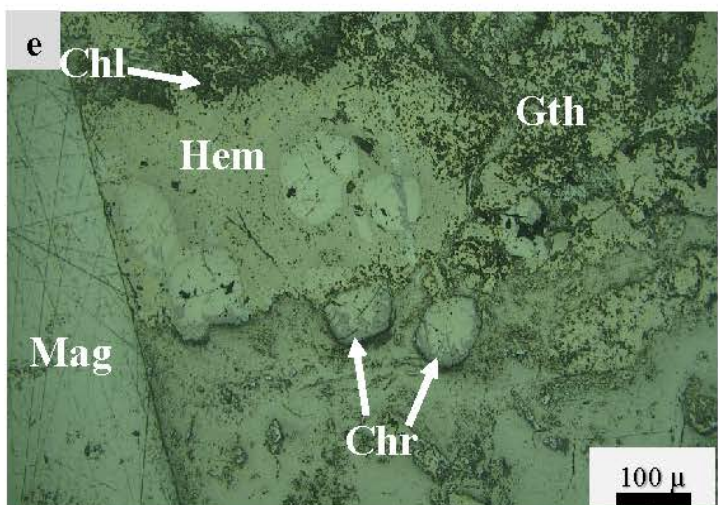
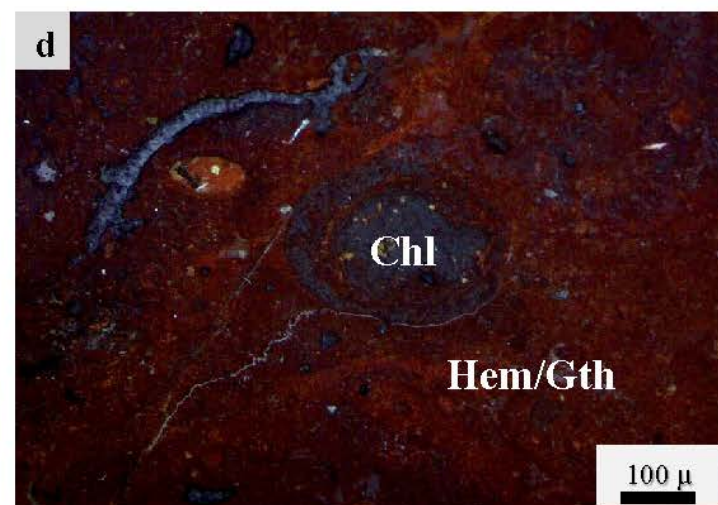
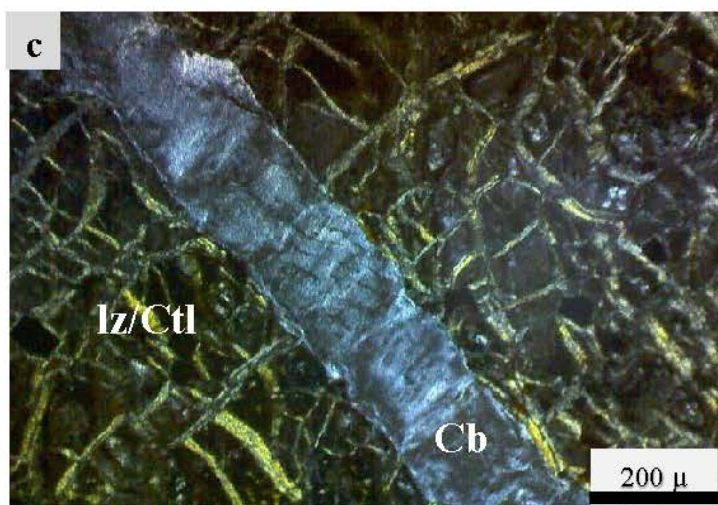
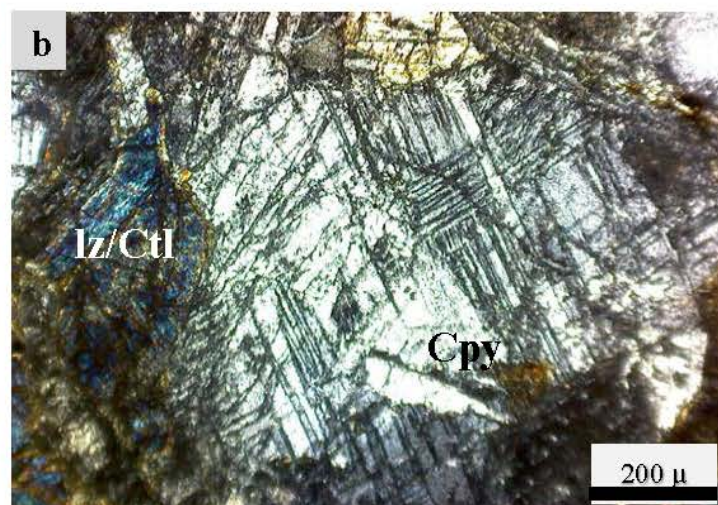
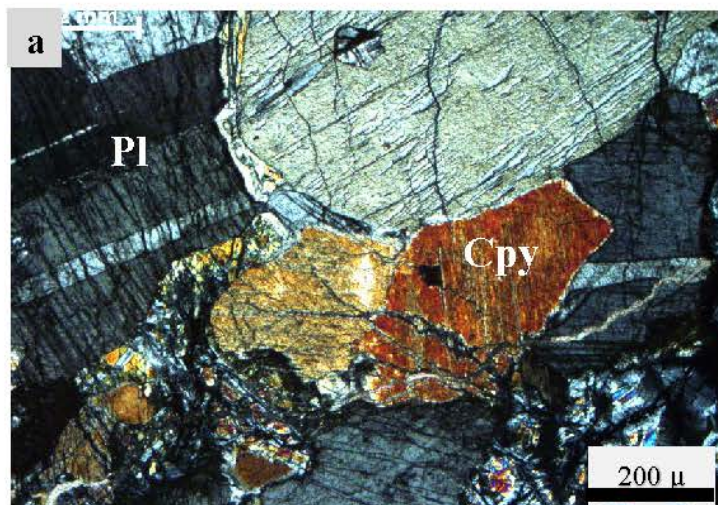
} Protolith



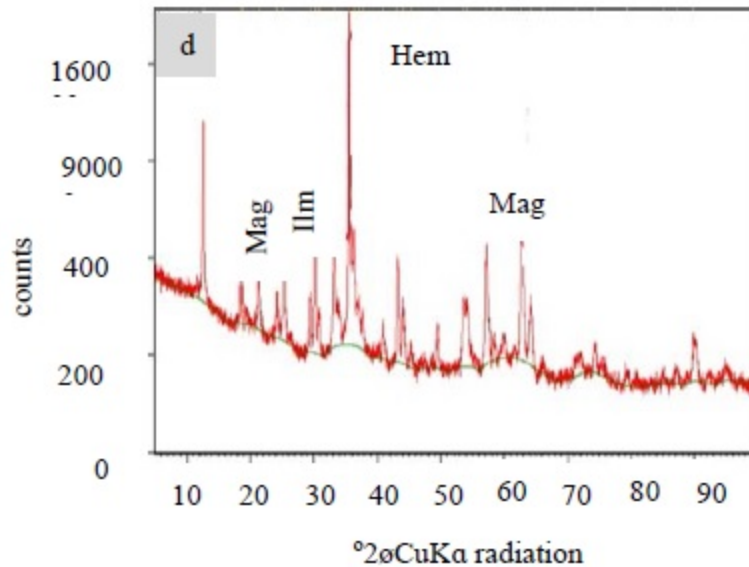
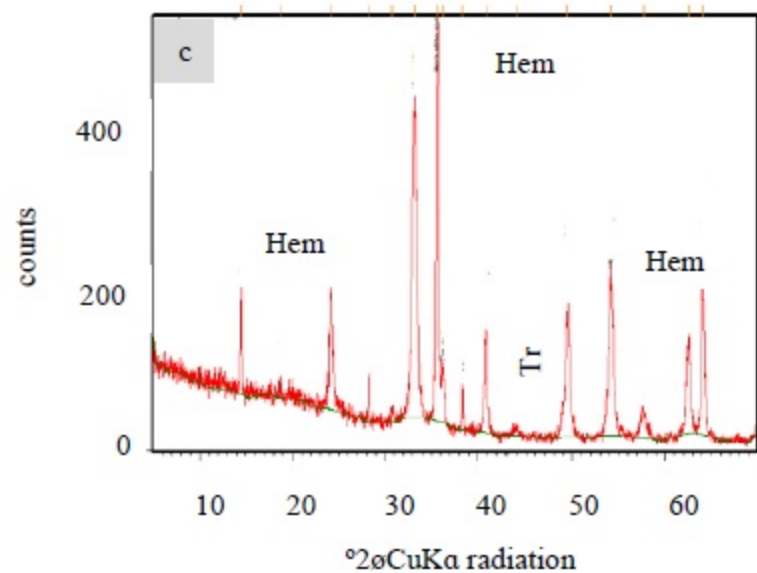
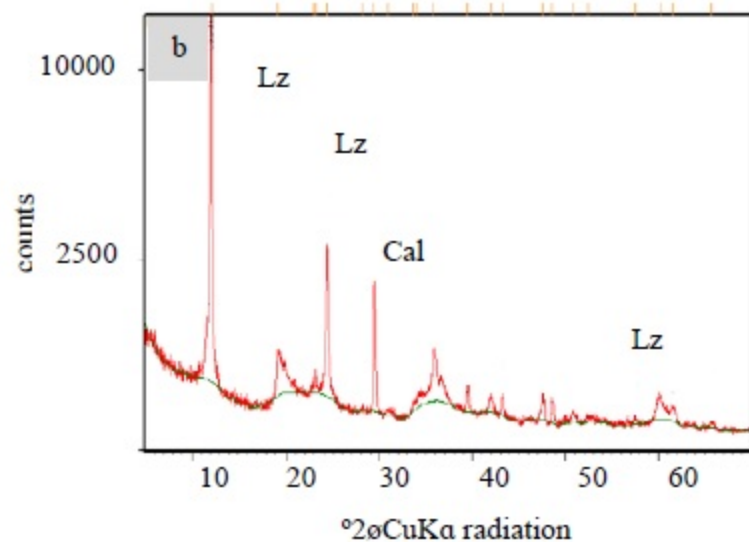
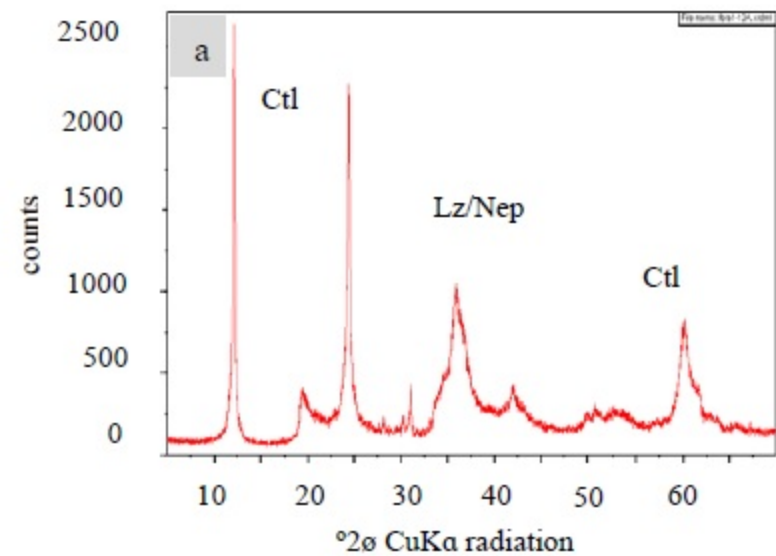
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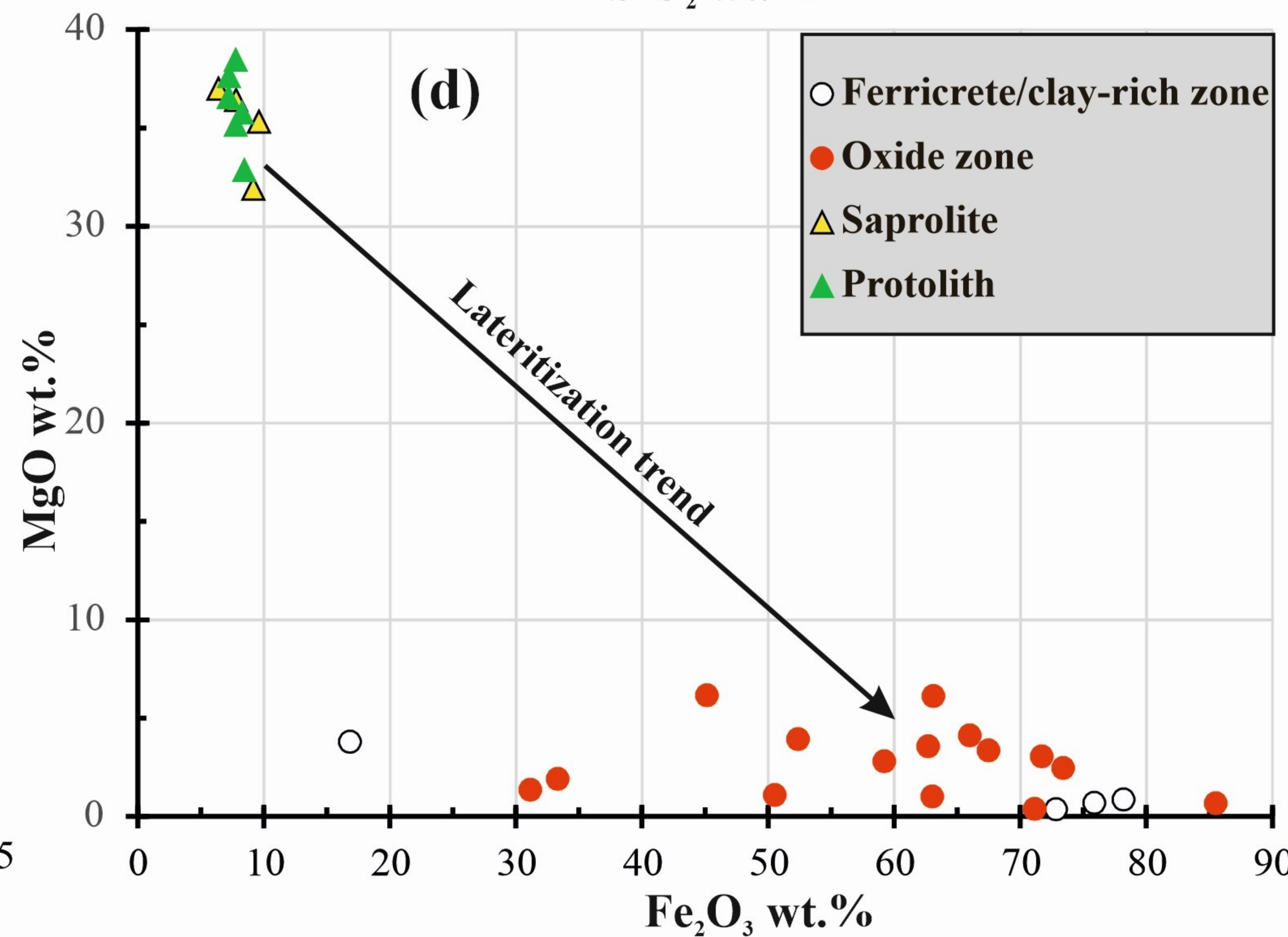
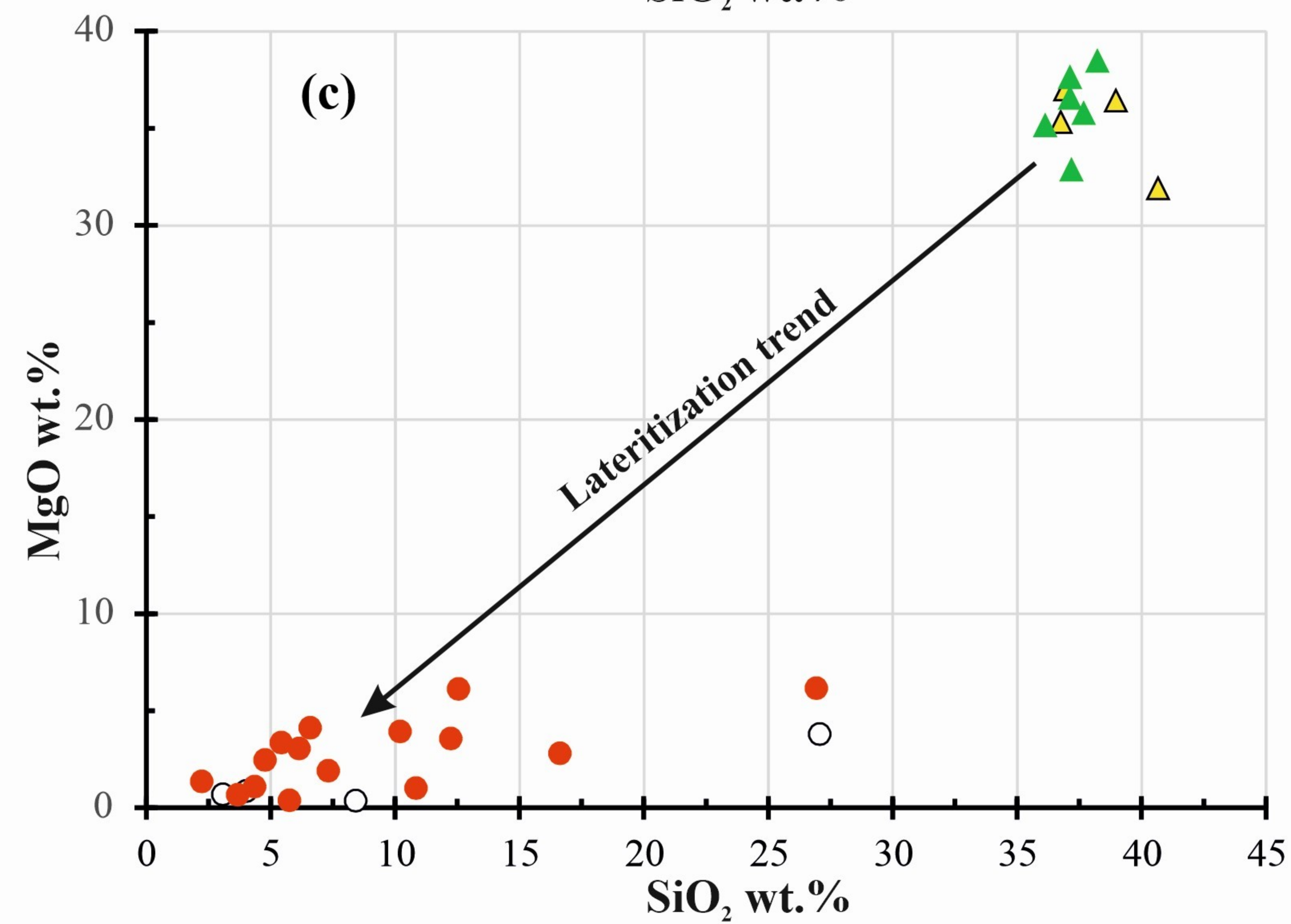
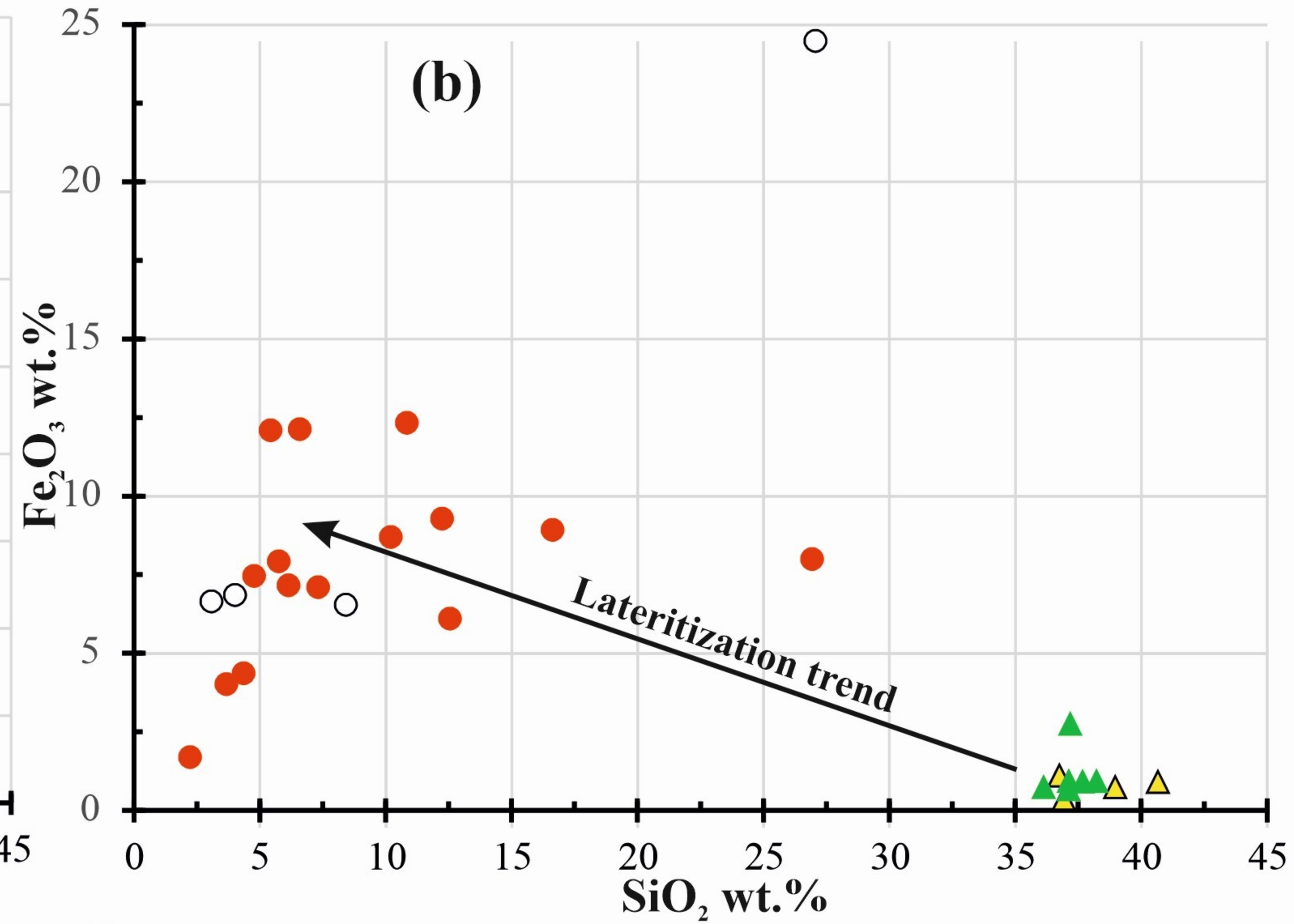
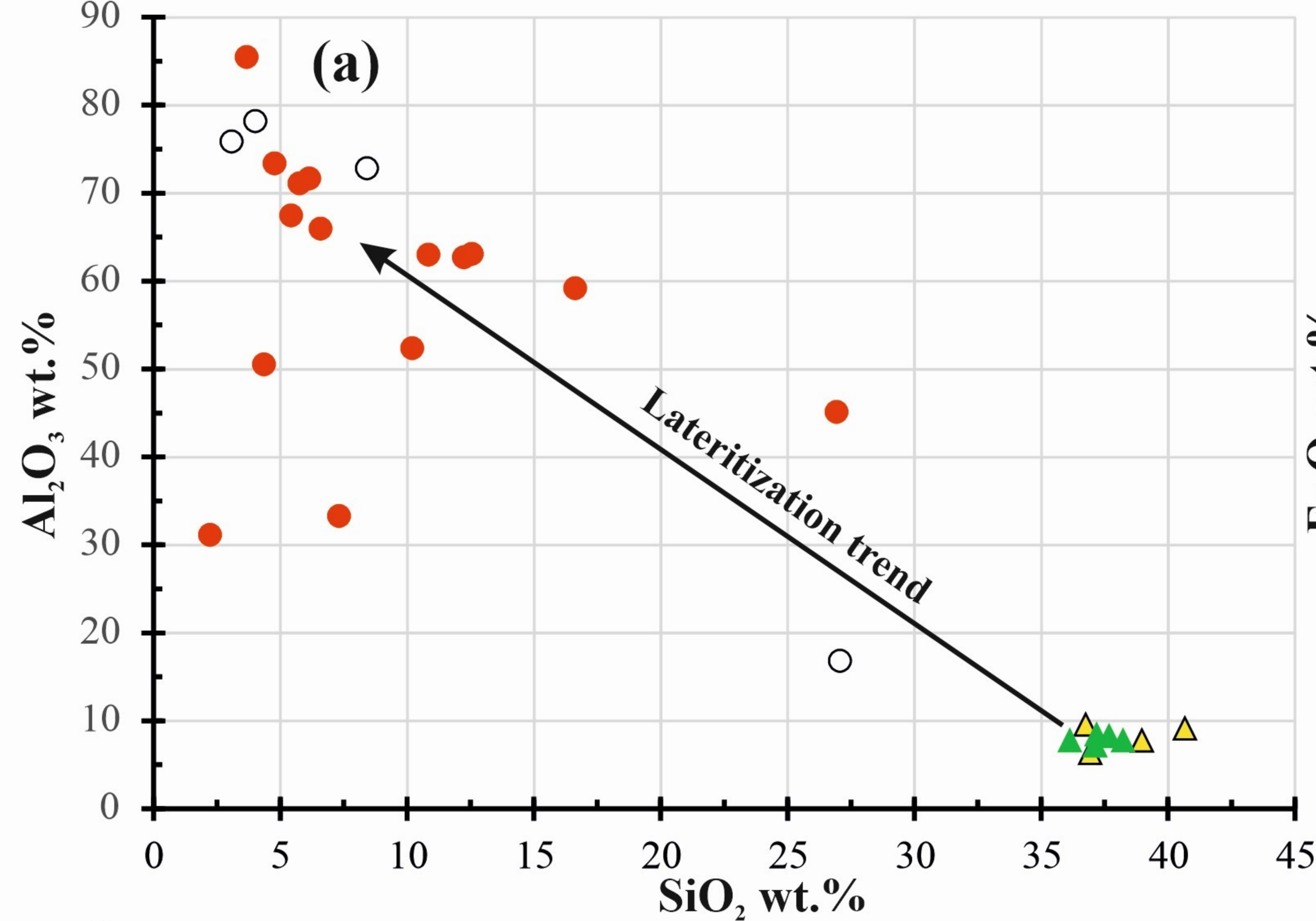


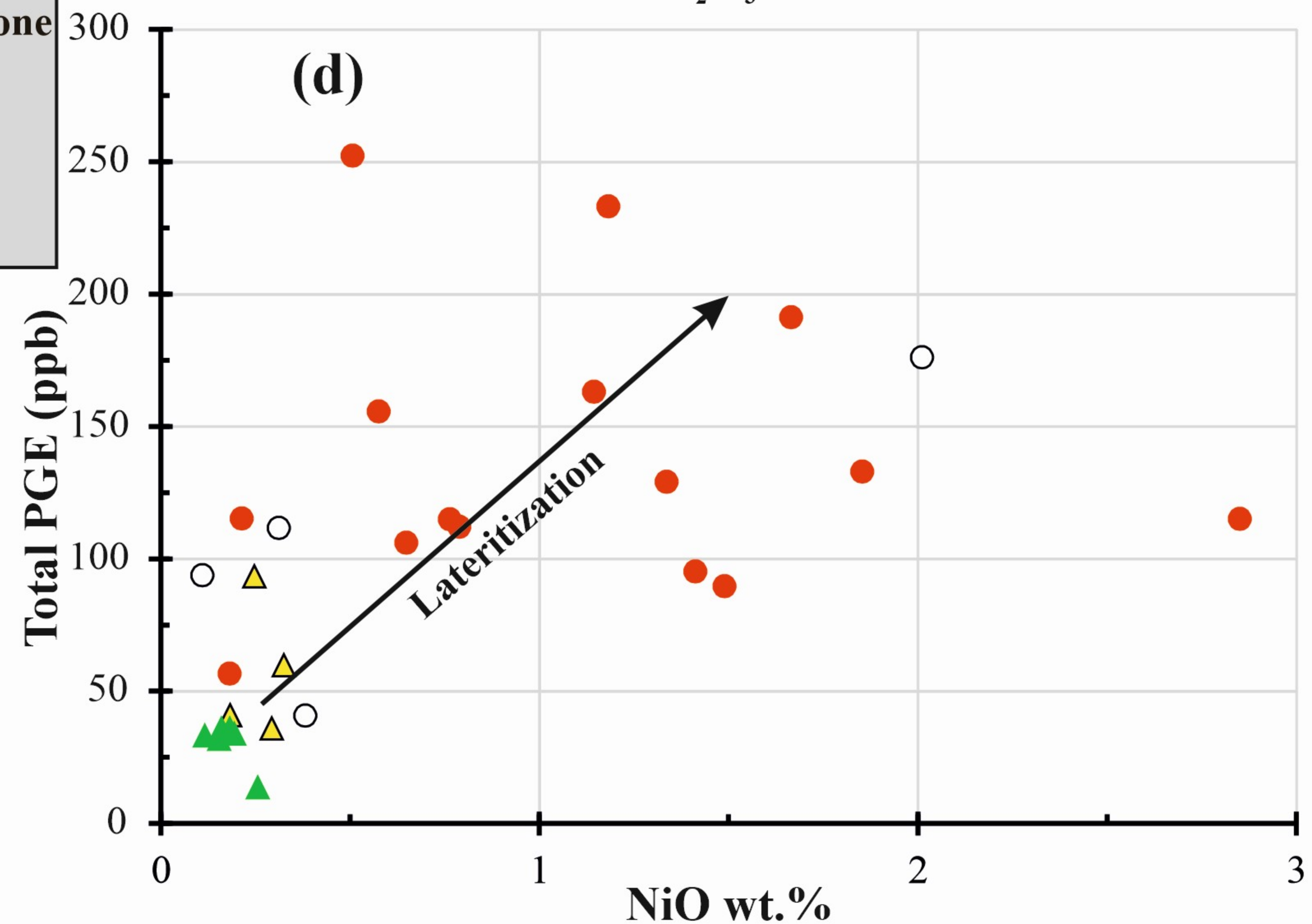
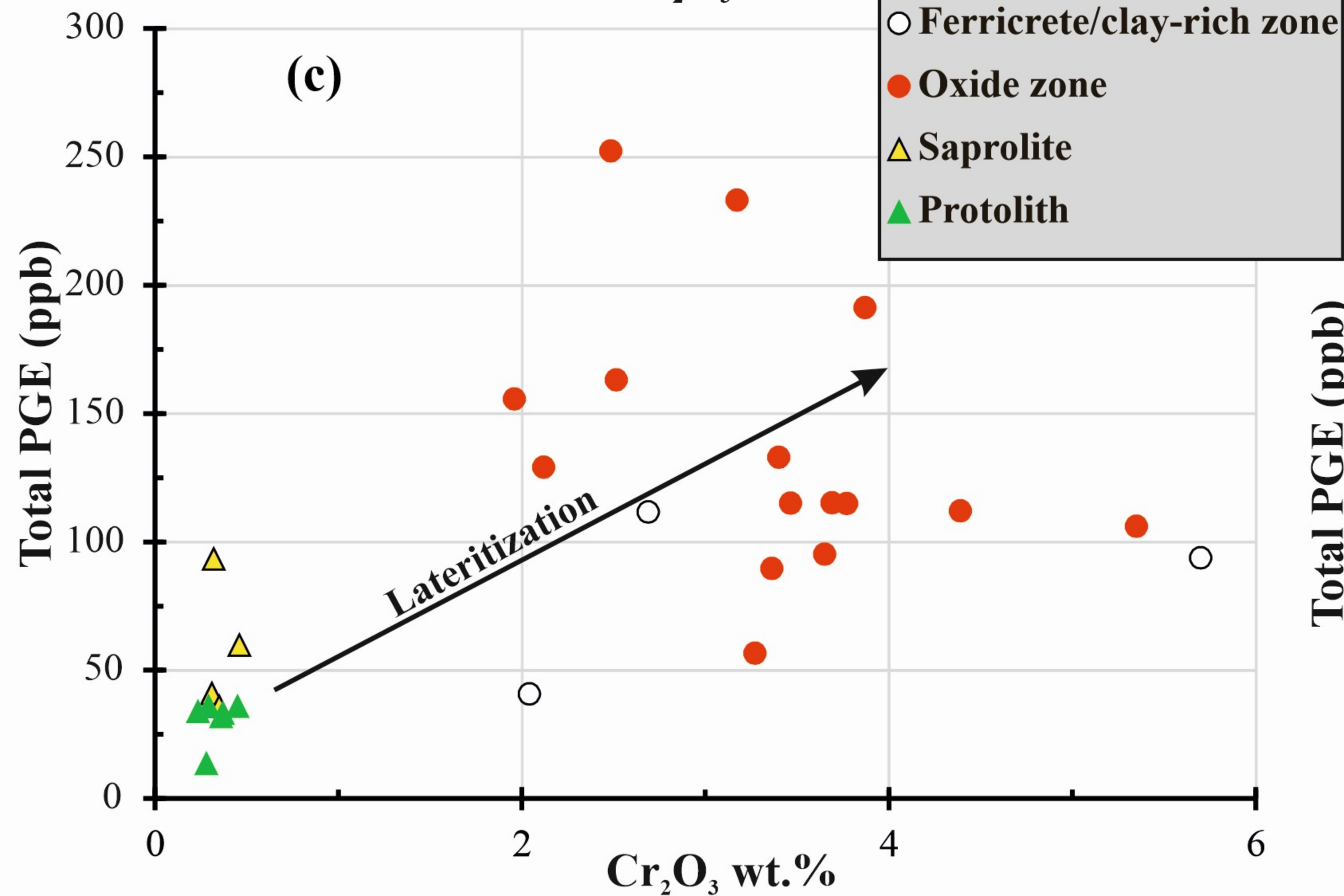
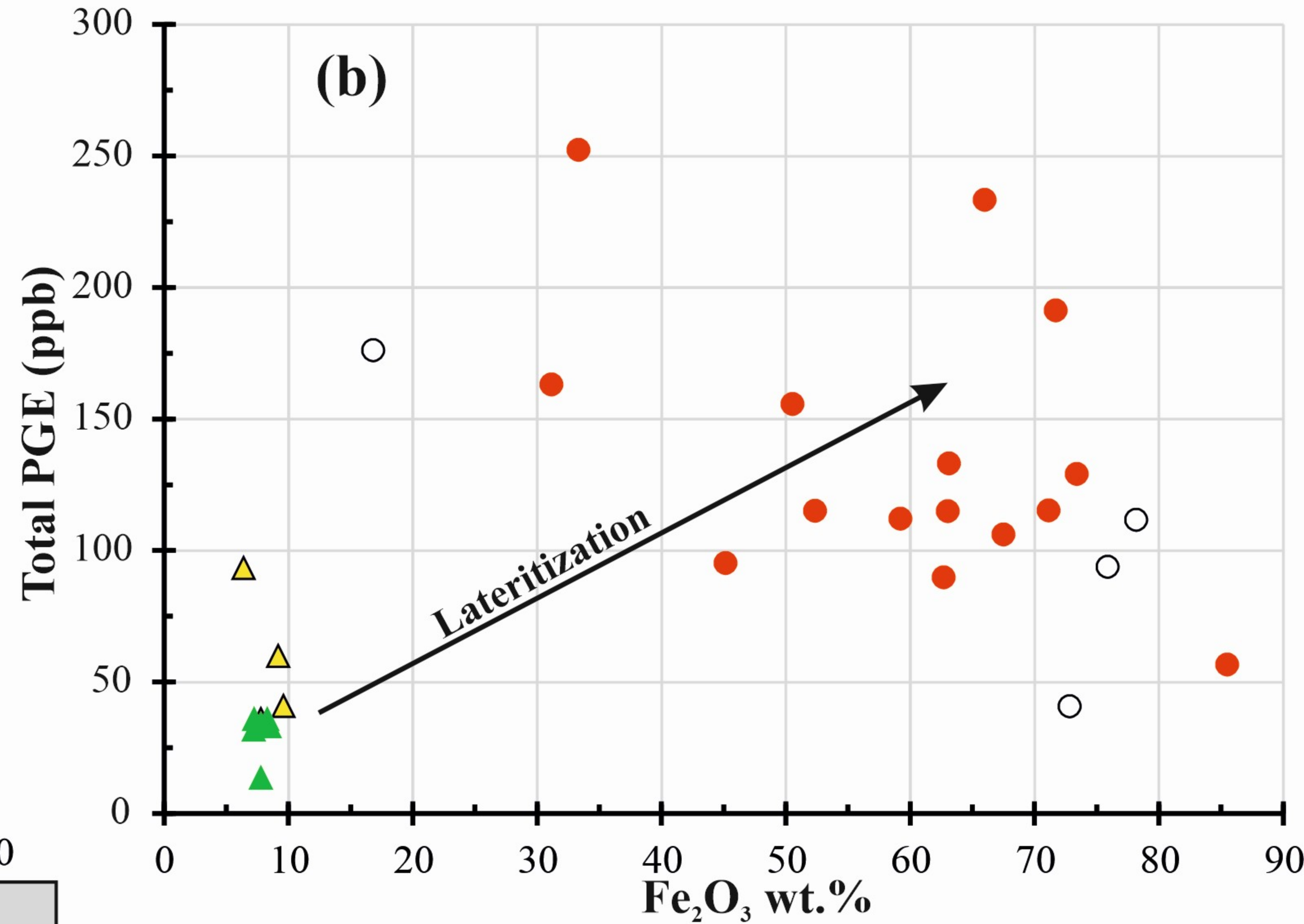
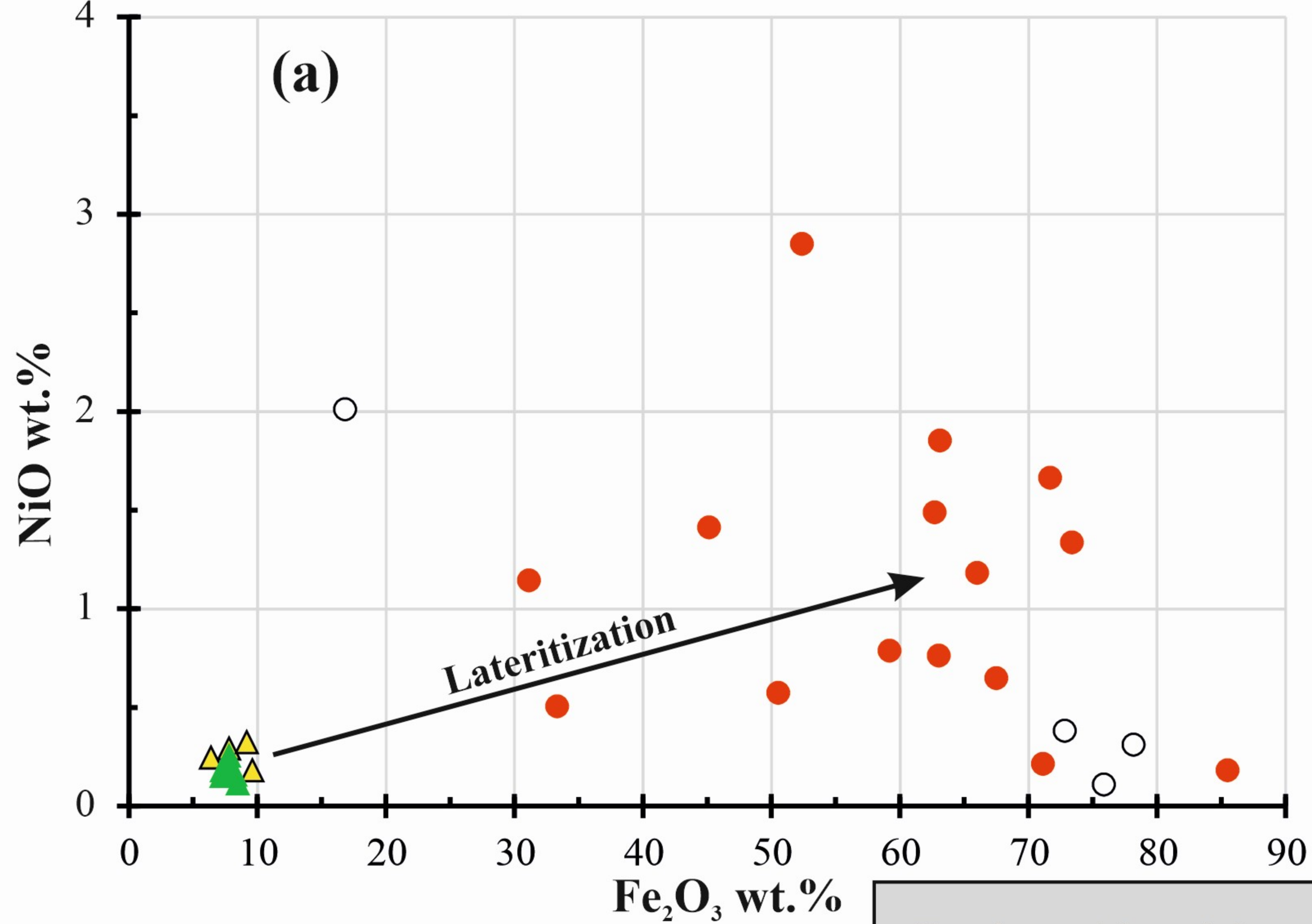
Sample locations

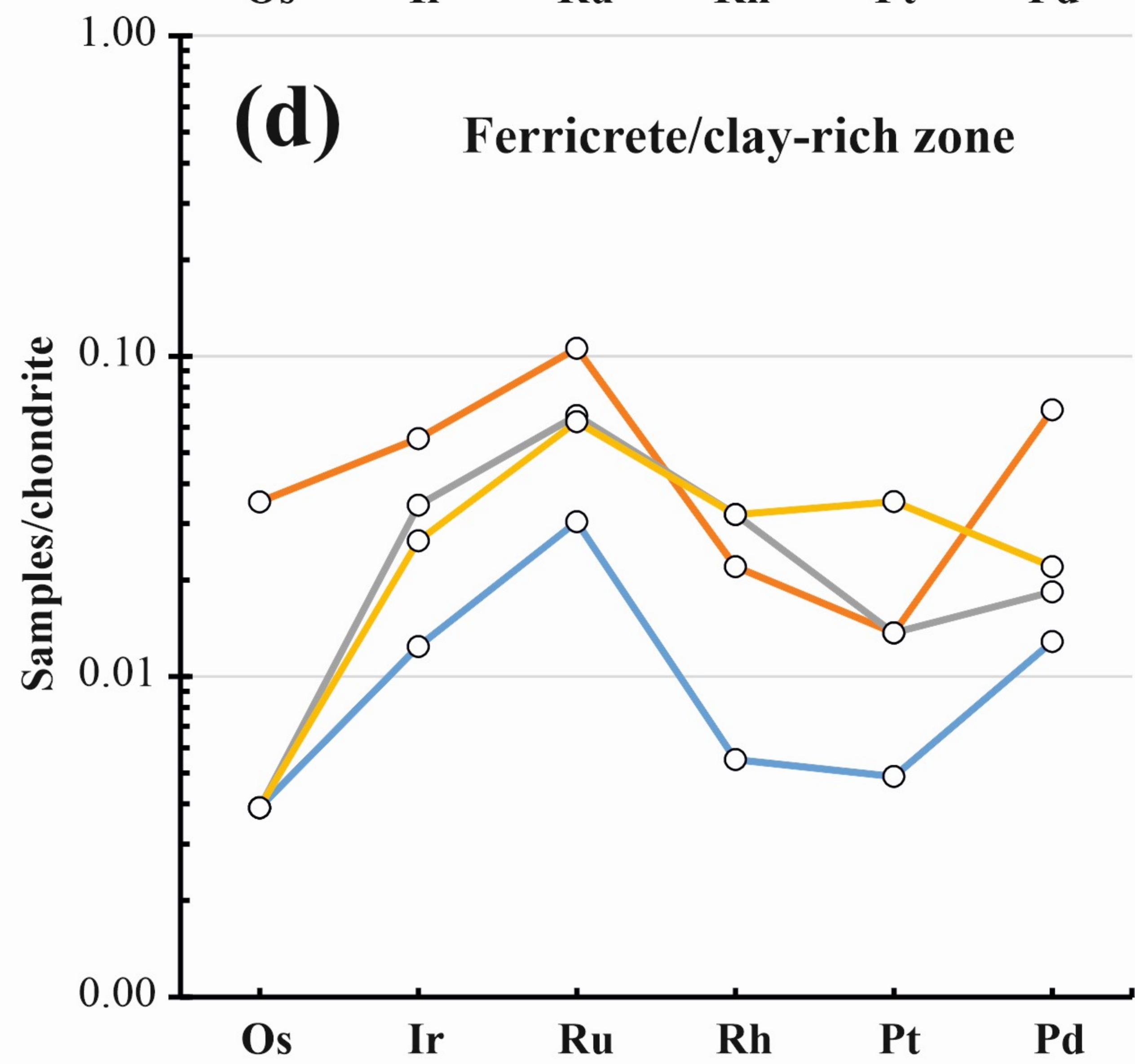
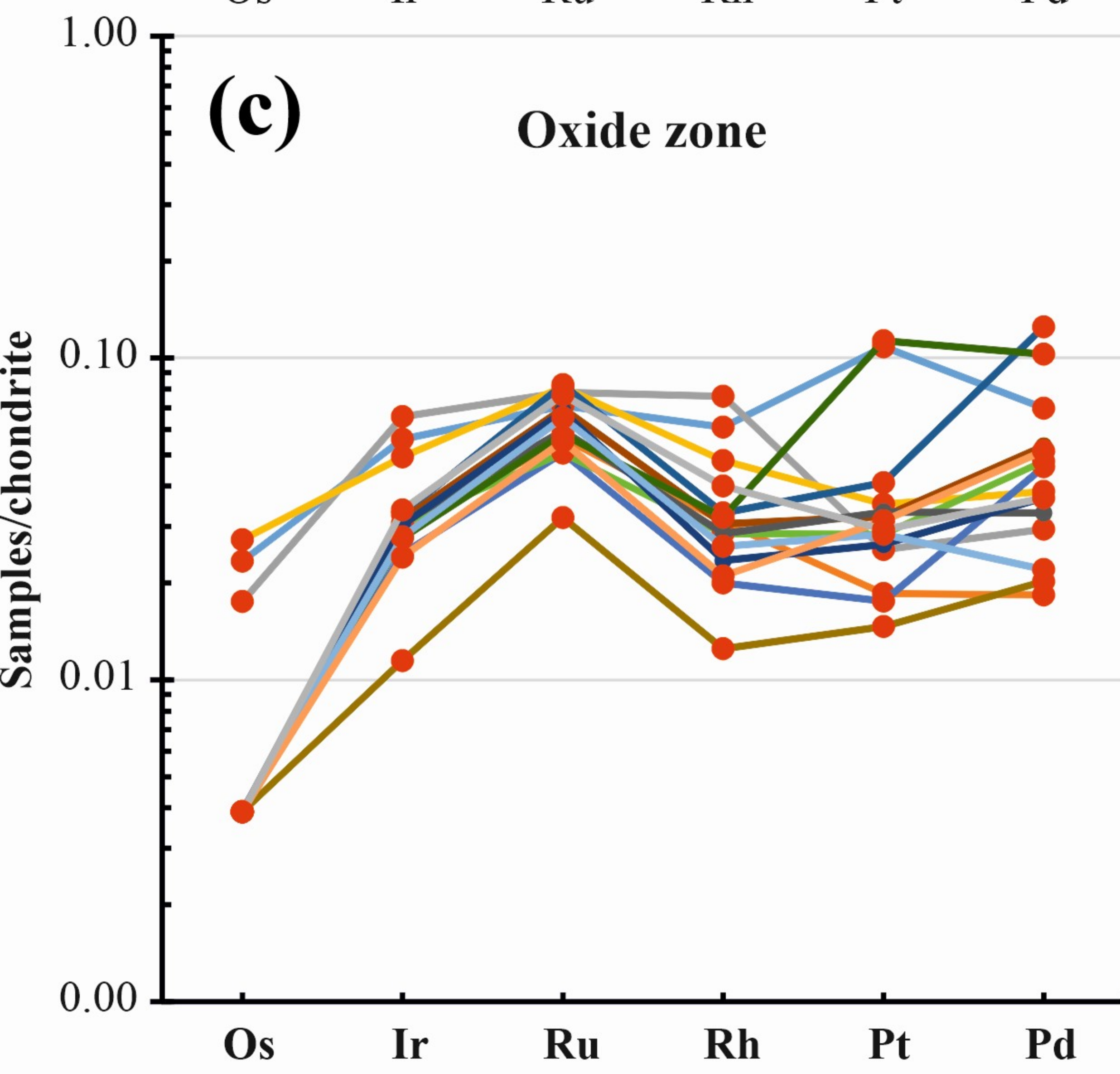
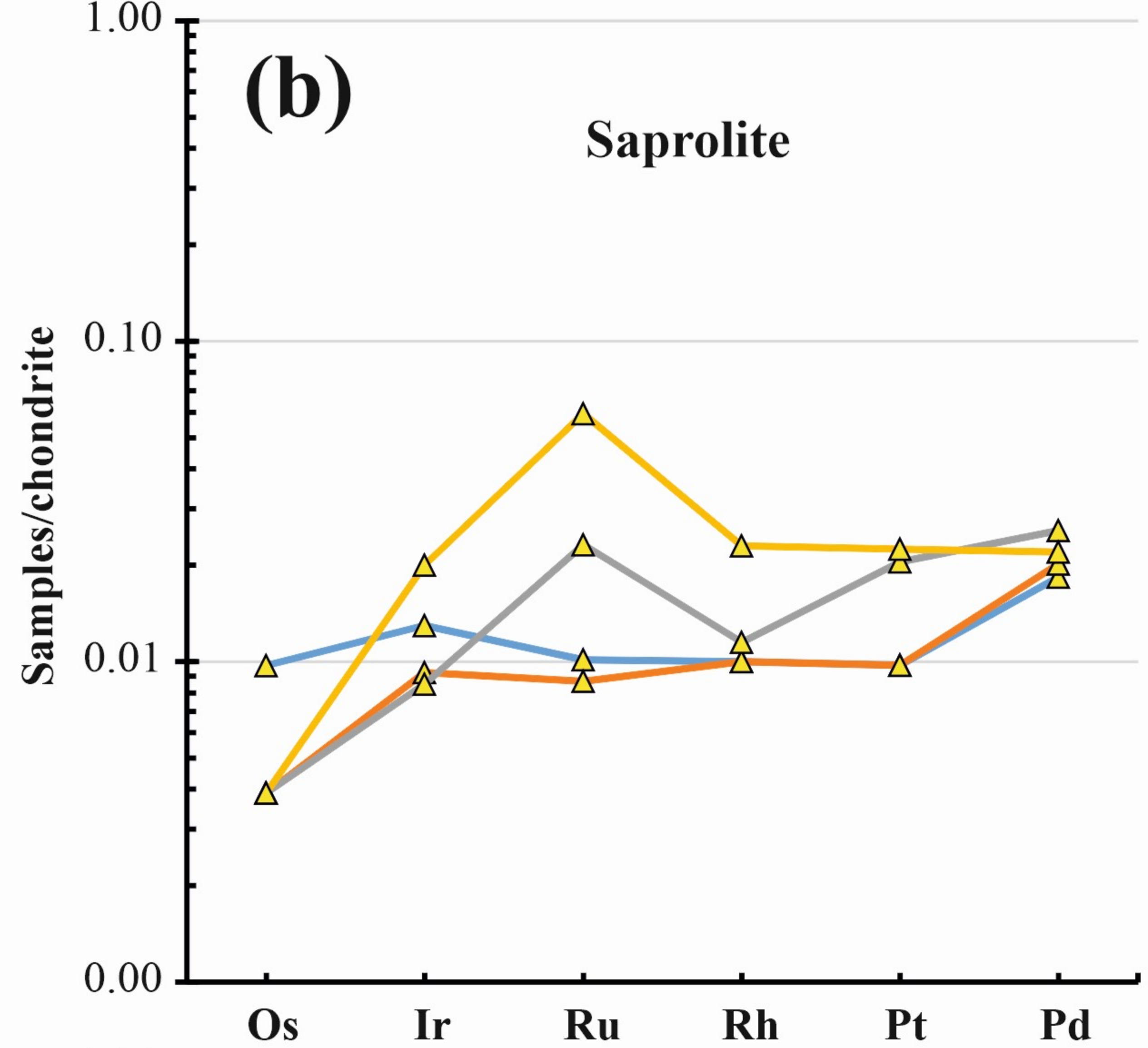
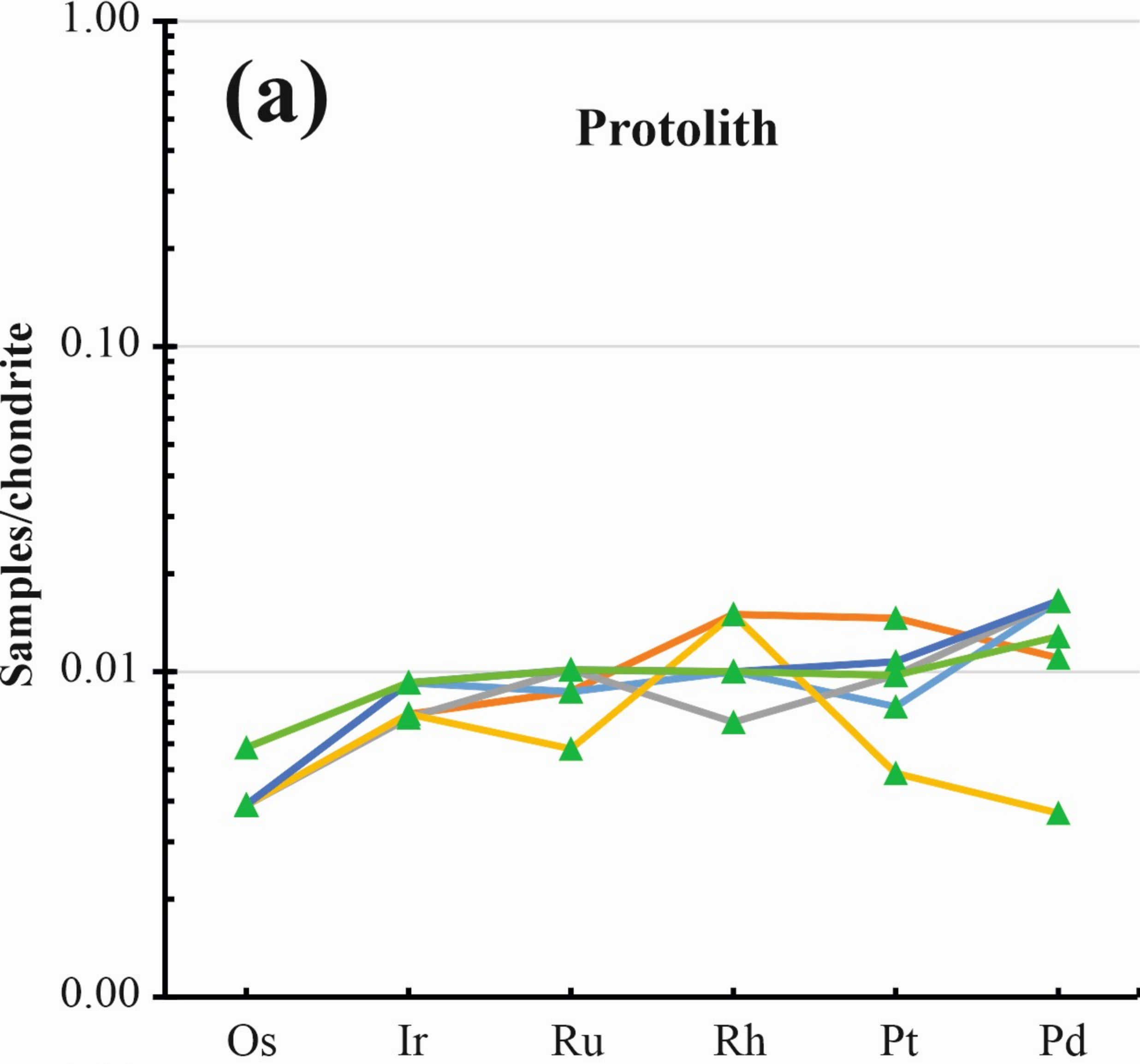


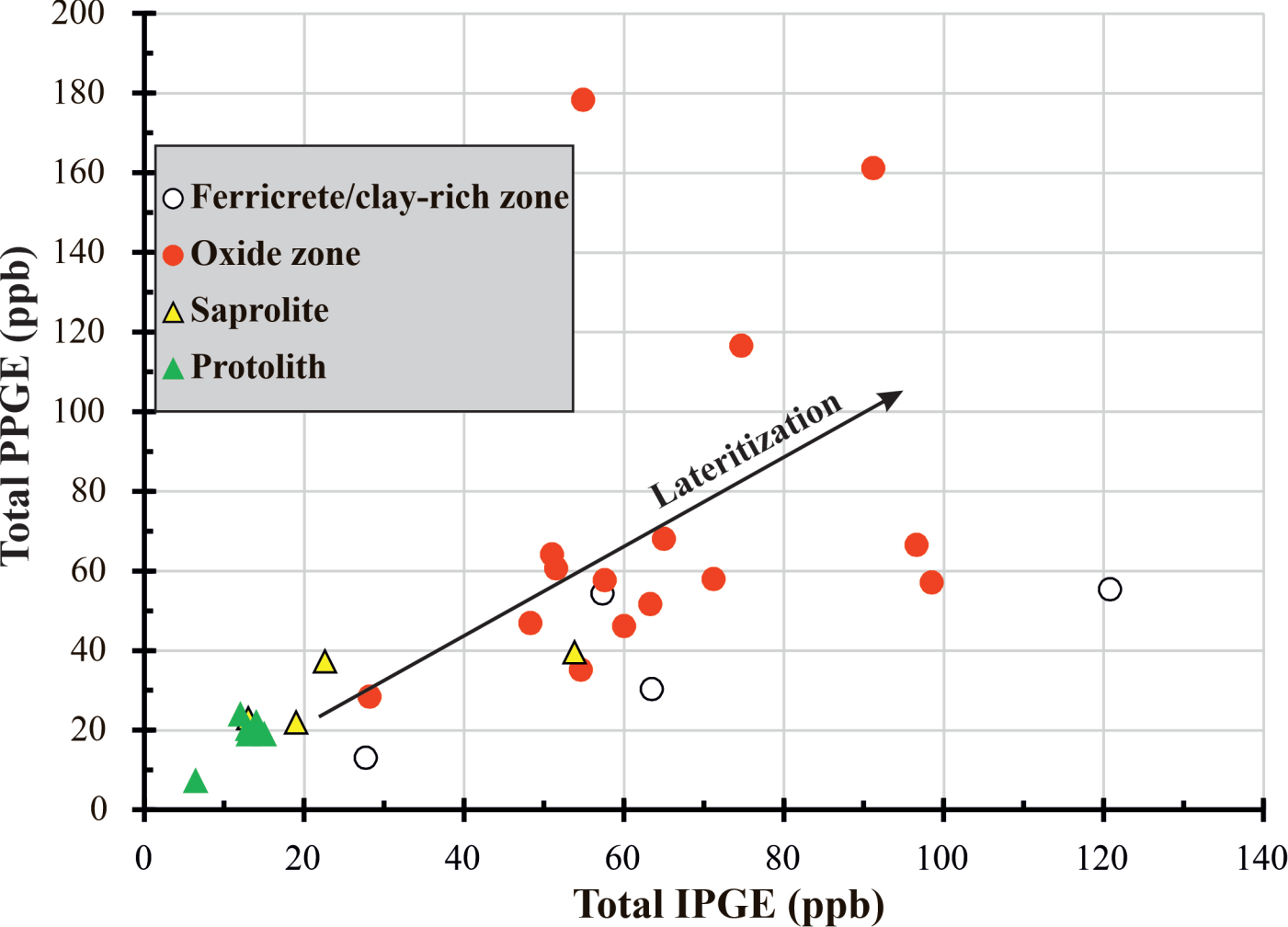


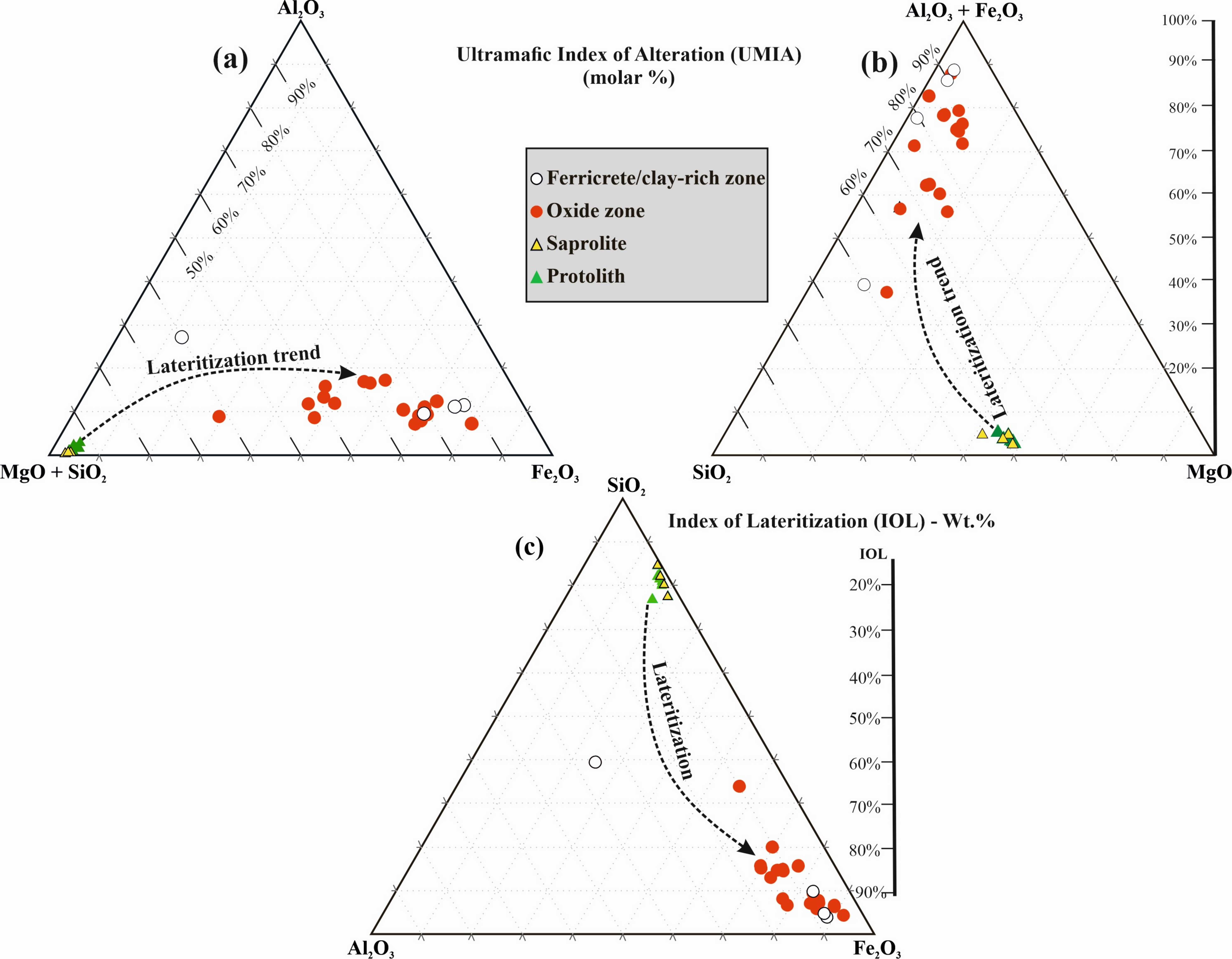


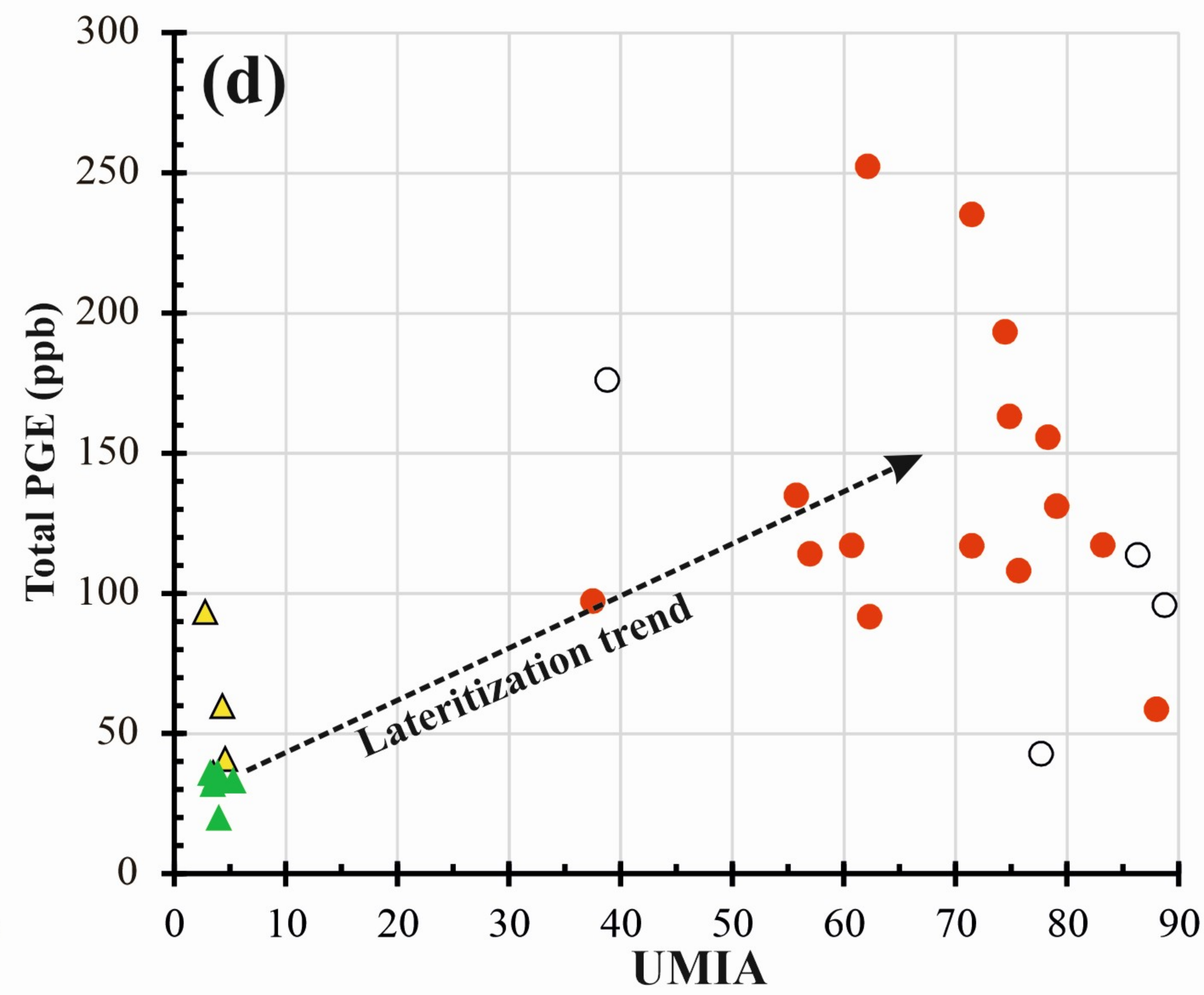
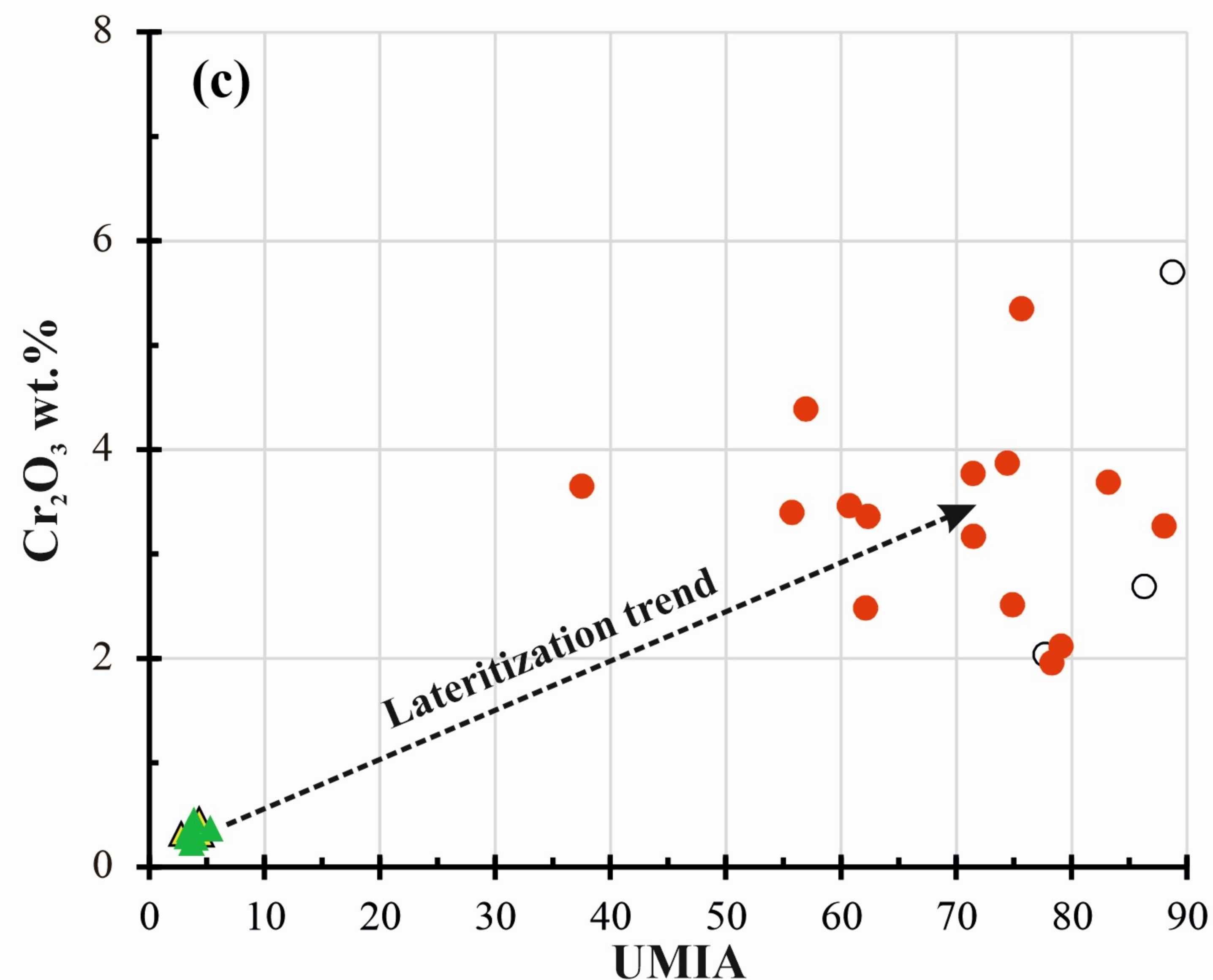
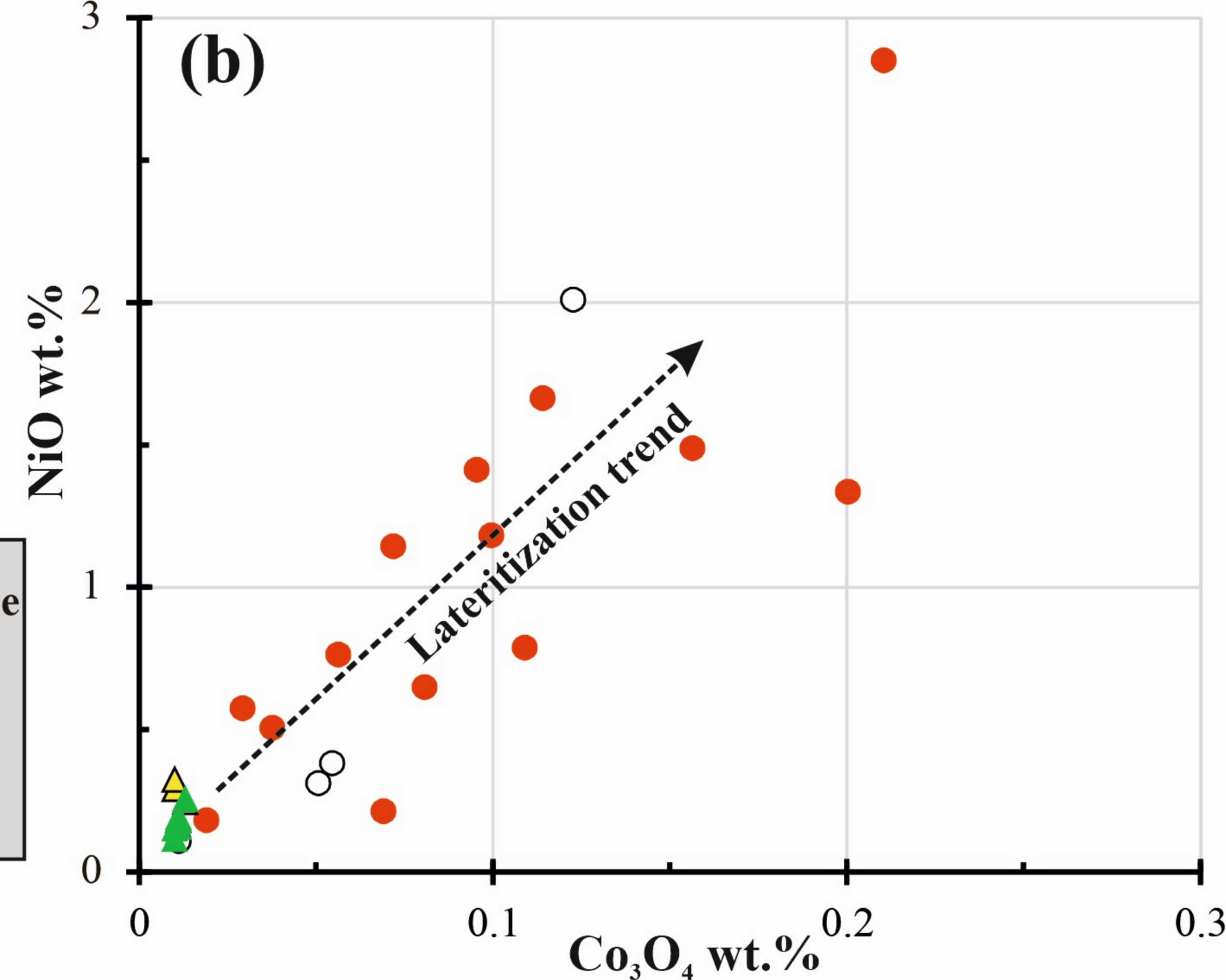
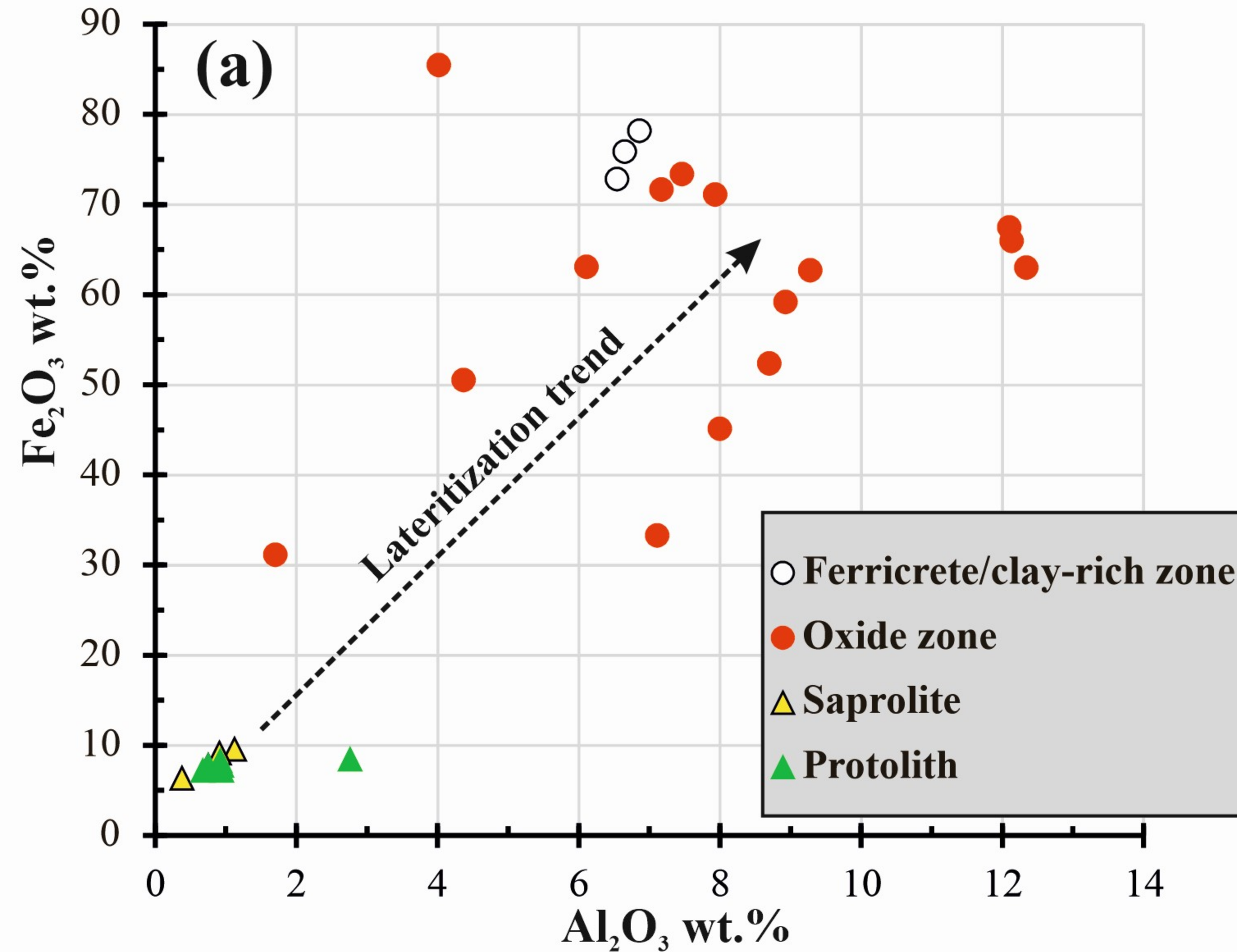












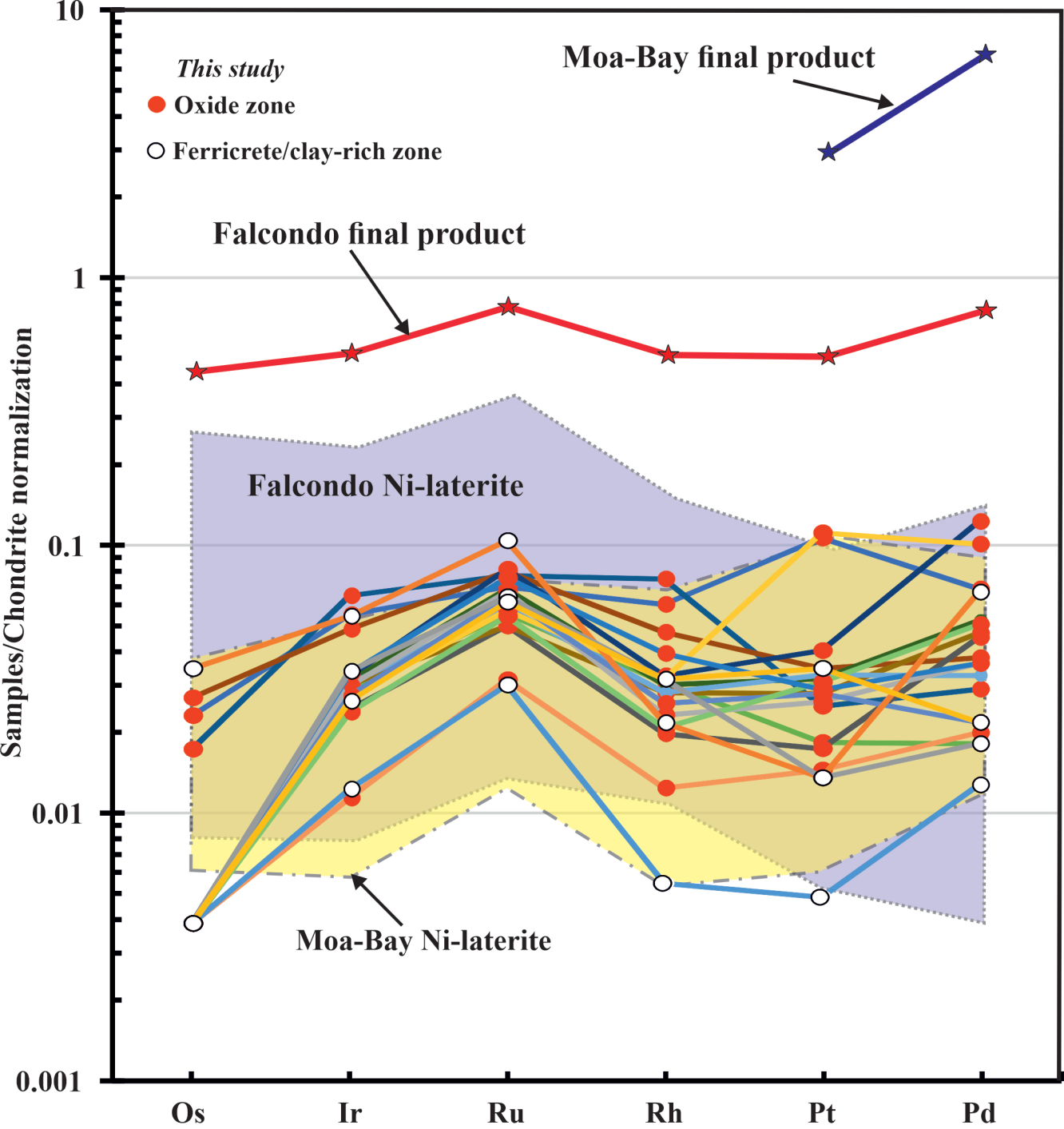


Table 1: Major, selected trace elements composition (wt.%), and PGE contents (ppb) of the protolith
UMIA = Ultramafic Index of Alteration. IOL - Index of Lateritization.

Profile# Zone	loc-1 Protolith		loc-2 Protolith	loc-3 and 4 Protolith	loc-5 Protolith	loc-6 Protolith	loc-1 saprolite
SiO ₂	37.67	37.11	37.17	38.21	37.11	36.12	36.74
Al ₂ O ₃	0.92	0.94	2.76	0.94	0.67	0.75	1.12
Fe ₂ O ₃ (T)	8.28	7.21	8.46	7.77	7.22	7.77	9.60
MnO	0.16	0.13	0.20	0.10	0.10	0.12	0.12
MgO	35.78	36.57	32.87	38.47	37.63	35.16	35.33
CaO	1.60	0.58	2.82	0.08	0.05	0.67	0.68
Na ₂ O	n.d.	n.d.	0.01	n.d.	n.d.	0.02	n.d.
K ₂ O	0.01	0.02	0.02	n.d.	0.00	0.09	0.01
TiO ₂	0.02	0.02	0.08	0.02	0.01	0.01	0.03
P ₂ O ₅	0.01	0.01	n.d.	0.05	n.d.	0.00	n.d.
Cr ₂ O ₃	0.45	0.36	0.37	0.28	0.29	0.23	0.31
NiO	0.16	0.15	0.12	0.26	0.18	0.19	0.18
Co ₃ O ₄	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LOI	15.72	16.18	15.67	14.72	15.20	15.10	15.81
Total	100.79	99.29	100.56	100.91	98.48	96.25	99.95
UMIA	4	3	5	4	3	4	5
IOL	4	3	5	4	3	4	5
PGE (ppb)							
Os	2	2	2	2	2	3	5
Ir	4	5	4	0.4	5	5	7
Ru	6	6	7	4	7	7	7
Rh	3	2	1	0.3	2	2	2
Pt	15	8	10	5	11	10	10
Pd	6	9	9	2	9	7	10
Au	n.d.	n.d.	3	1.4	n.d.	n.d.	n.d.
Σ PGE	36	32	33	14	36	34	41
Σ IPGE	12	13	13	6	14	15	19
Σ PPGE	24	19	20	7	22	19	22
Pd/IrN	1.49	1.78	2.18	4.95	2.29	1.78	1.42
Ru/PtN	0.59	1.11	0.89	1.48	1.04	0.95	1.04

and saprolite samples of the studied Ni-laterite profiles of the Oman ophiolite.

loc-2 saprolite	loc-3 and 4 saprolite	
38.96	40.66	36.92
0.75	0.91	0.38
7.78	9.16	6.39
0.11	0.12	0.09
36.43	31.91	37.00
0.76	1.19	3.25
0.01	0.01	0.01
0.01	0.03	0.01
0.01	0.02	0.01
0.01	0.05	0.04
0.35	0.46	0.32
0.29	0.33	0.25
0.01	0.02	0.01
14.60	15.88	15.86
100.09	100.74	100.54
3	4	3
4	4	3
2	2	2
5	5	11
6	16	41
2	2	5
10	21	23
11	14	12
n.d.	5	1
36	60	93
13	23	54
23	37	40
1.39	3.02	1.10
1.04	1.13	2.65

Table 2: Major, selected trace elements composition (wt.%), and PGE contents of the oxide and clay-rich zone
UMIA = Ultramafic Index of Alteration. IOL - Index of Lateritization.

Profile#	loc-1						loc
Zone	oxide zone				ferricrete/clay-rich		oxide
SiO ₂	7.32	12.24	4.35	2.23	8.42	27.06	26.93
Al ₂ O ₃	7.11	9.28	4.37	1.70	6.54	24.49	8.00
Fe ₂ O ₃ (T)	33.31	62.70	50.53	31.14	72.82	16.82	45.14
MnO	0.54	0.18	0.65	2.52	0.18	0.18	0.46
MgO	1.93	3.57	1.10	1.37	0.37	3.80	6.18
CaO	24.30	1.33	18.59	30.31	0.20	1.30	0.61
Na ₂ O	0.06	0.06	0.04	0.21	0.10	0.14	0.06
K ₂ O	0.02	0.03	0.01	0.01	0.01	0.84	0.05
TiO ₂	0.08	0.09	0.06	0.03	0.11	0.57	0.21
P ₂ O ₅	0.04	0.01	0.01	0.01	0.03	0.01	0.01
Cr ₂ O ₃	2.48	3.36	1.96	2.51	2.04	11.44	3.65
NiO	0.51	1.49	0.58	1.14	0.38	2.01	1.41
Co ₃ O ₄	0.04	0.16	0.03	0.07	0.05	0.12	0.10
LOI	22.41	6.37	16.67	25.62	8.02	12.59	7.11
Total	100.15	100.86	98.94	98.88	99.28	101.37	99.92
UMIA	62	62	78	75	78	39	38
IOL	74	71	86	80	86	53	41
PGE (ppb)							
Os	12	2	9	14	2	18	2
Ir	30	16	36	27	7	30	13
Ru	49	39	54	56	21	73	35
Rh	12	6	15	10	1	4	4
Pt	111	19	26	36	5	14	18
Pd	38	10	16	21	7	37	25
Au	2	2	4	3	1	15	3
Σ PGE	252	92	156	163	43	176	97
Σ IPGE	91	57	99	97	30	121	50
Σ PPGE	161	35	57	67	13	55	47
Pd/IrN	1.25	0.64	0.45	0.78	1.04	1.23	1.86
Ru/PtN	0.66	3.05	3.09	2.31	6.24	7.75	2.89

samples of the studied Ni-laterite profiles of the Oman ophiolite.

loc-2	loc-3 and 4		loc-5				
zone	oxide zone		oxide zone			ferricrete/clay-rich	
16.62	6.14	12.55	5.75	3.67	10.84	3.08	4.01
8.93	7.17	6.11	7.93	4.02	12.34	6.65	6.86
59.20	71.69	63.11	71.13	85.50	63.02	75.87	78.18
0.31	0.26	0.19	0.10	0.04	0.11	0.05	0.12
2.81	3.07	6.14	0.40	0.69	1.03	0.70	0.87
0.39	0.47	0.32	0.06	0.07	0.29	0.51	0.92
0.05	0.01	0.01	0.45	0.01	0.09	0.08	0.20
0.02	0.02	0.03	0.10	0.01	0.01	0.01	0.01
0.19	0.06	0.26	0.24	0.11	0.11	0.13	0.17
0.03	0.06	0.05	0.12	0.08	0.06	0.09	0.06
4.39	3.87	3.40	3.69	3.27	3.77	5.70	2.69
0.79	1.67	1.85	0.21	0.18	0.76	0.11	0.31
0.11	0.11	0.50	0.07	0.02	0.06	0.01	0.05
4.99	5.17	6.06	10.42	3.23	10.67	10.46	4.87
98.83	99.77	100.58	100.67	100.90	103.16	103.45	99.32
57	74	56	83	88	71	89	86
64	83	60	95	94	86	99	96
2	2	2	2	2	2	2	2
17	18	17	17	6	16	19	14
35	57	48	41	22	47	45	43
6	7	6.1	6	3	5	6	6
29	42	33	34	15	27	14	36
26	68	29	18	11	20	10	12
2	8.6	0.8	3	3	1	1	1
114	193	135	117	59	117	96	114
54	77	67	60	30	65	66	59
61	117	68	58	29	52	30	54
1.56	3.81	1.69	1.07	1.76	1.22	0.54	0.83
1.79	2.02	2.16	1.79	2.18	2.59	4.77	1.77

loc-6			
oxide zone			
6.59	5.43	10.20	4.78
12.13	12.10	8.70	7.46
65.99	67.49	52.36	73.39
0.32	0.19	0.17	0.33
4.14	3.37	3.94	2.48
1.88	1.28	6.36	2.81
0.03	0.05	0.17	0.05
0.01	0.01	0.02	0.01
0.16	0.14	0.04	0.07
0.01	0.01	0.01	0.01
3.17	5.35	3.46	2.12
1.18	0.65	2.85	1.34
0.10	0.08	0.21	0.20
4.87	4.27	10.65	4.48
100.58	100.42	99.15	99.53
71	76	61	79
85	91	69	89
2	2	2	2
15	15	13	18
40	45	38	53
6	5	4	8
116	29	32	30
56	12	28	20
1	1	1	1
235	108	117	131
57	62	53	73
178	46	64	58
3.72	0.79	2.13	1.09
0.51	2.31	1.76	2.62