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Mineral Composition and Environmental Importance of Fe–Mn Nodules in Soils in Karst Areas of Guangxi, China

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Abstract: The mineral composition of Fe–Mn nodules (FMNs) is closely related to the environment in which FMNs are formed. The formation mechanism of FMNs has consistently been one of the major topics in related research. In this study, the mineral composition of FMNs in soils derived from carbonate rocks in typical karst areas with high geochemical background in Guangxi, Southwest China, was investigated. The results showed that $\text{Fe}_2\text{O}_3$ (30.06%), $\text{SiO}_2$ (19.72%), $\text{Al}_2\text{O}_3$ (17.93%), $\text{TiO}_2$ (0.96%), $\text{P}_2\text{O}_5$ (0.78%), and $\text{MnO}_2$ (0.64%) were the main elemental composition, while four alkaline oxides $\text{K}_2\text{O}$, $\text{Na}_2\text{O}$, $\text{CaO}$, and $\text{MgO}$ were less than 0.5% in soil FMNs. In addition, 10 mineral types were identified in soil FMNs in the study area, namely quartz, goethite, clinochlore, illite, kaolinite, boehmite, albite, microcline, lithiophorite, and hematite. There were no obvious differences in the mineral composition of soil FMNs in the study area compared with those observed in non-karst areas worldwide. The formation process of FMNs can be determined based on the surrounding environment that affects the soil mineral composition. The results suggested a relatively complex formation mechanism of soil FMNs. Moreover, both primary and secondary minerals were found in soil FMNs. However, some minerals can exist stably under normal redox conditions, while the other part of minerals can be easily weathered and dissolved, indicating a relatively high formation rate of soil FMNs and a relatively stable internal environment.

Keywords: Fe–Mn nodules; karst area; mineral composition; formation mechanism; Guangxi

1. Introduction

Iron (Fe) and manganese (Mn) are important elements of the parent rock and soils. They exist predominantly as oxides, hydroxides, and oxyhydroxides, and have multiple redox states and can therefore function as both electron donors and electron acceptors in soils [1]. The Fe–Mn nodules (FMNs) are discrete materials consisting of soil or sediment materials cemented together under the influence of Fe and Mn oxides [2,3]. Indeed, soil FMNs are important bodies in soil element migration and enrichment under certain redox conditions [4–6]. They are widely distributed in the terra rossa formation in karst areas [7–9]. In fact, soil with a high geochemical background refers to soil containing large amounts of heavy metals (e.g., Cd, As, Pb, and Hg) as a result of geogenic processes rather than anthropogenic activities, including parent rock weathering and subsequent pedogenic processes [10]. The karst area is one of the typical geologically high background areas that are receiving increasing attention from researchers worldwide [8,10–12]. Moreover, the high geological background leads to ecological and environmental problems,
including soil heavy metals contamination, thereby attracting increasing attention from researchers [11,12]. A geochemical survey of cultivated land in China showed that the southwestern karst area, including Yunnan, Guizhou, and Guangxi Provinces, is one of the most polluted areas [13]. Previous studies have revealed that although the contents of heavy metal contents in the original carbonate rocks in the southwestern karst area in China are relatively low, secondary enrichment may occur during the weathering process, leading to abnormal enrichments of soil heavy metal elements [9,14]. In karst areas, the parent rocks consist generally of carbonate rocks, specifically limestone and dolomite, with small quantities of other rock types [3,8,10–12]. In addition, research on the FMNs in karst areas considered several aspects, including chemical composition, ecological risk, element migration characteristics, and isotopes of the FMNs [3–5,8].

Numerous studies have focused on the mineralogical types, micromorphological characteristics, element composition, formation mechanisms, ecological risk assessment, and environmental importance of FMNs [2,3,15,16]. The soil mineral composition is mainly affected by the parent material, soil formation process, and environmental factors (e.g., biological, redox and climatic conditions), resulting in significantly different soil physico-chemical properties [17–21]. Indeed, although numerous researchers have revealed that FMNs were formed as a result of the long-term evolution of the formed soil in non-karst areas [2,15,16], the mineral composition and environmental importance of FMNs have rarely been discussed. Therefore, investigating the composition and environmental importance of FMNs provides further insights into the formation mechanism of soil FMNs in karst areas. Previous studies have highlighted that primary minerals record the characteristics of the original parent material prior to soil formation, while secondary minerals provide evidence of soil formation, which may be helpful for understanding the soil composition from the perspective of soil genesis [2,15]. Therefore, by assessing the characteristics of soil secondary minerals, the genetic characteristics of soil, formation mechanism, soil-forming environment, and the degree of soil weathering can be determined. Indeed, research on soil secondary minerals has attracted considerable interest from soil and environmental scientists worldwide. In China, studies on secondary minerals of FMNs have considered mainly the red soils of South China and the Loess Plateau, while systematic research on FMNs in Southwest China, especially in karst areas, is still relatively weak. The mineral composition in the soil was closely related to its formation condition, which can further help us to understand the relationship between minerals and environment and the formation of FMNs.

Systematic studies on the mineral composition of FMNs may be helpful for understanding the environmental conditions favoring their formation and for reconstructing the soil in karst areas. The environmental conditions may affect the mineral composition of FMNs. Therefore, the main objective of the current study is to assess the mineral composition of FMNs in soils in karst areas and to understand the environmental conditions using X-ray powder diffraction. In addition, the mineral composition of FMNs in the karst area was compared to those in non-karst areas to reveal the relationship between mineral composition and its forming environment.

2. Materials and Methods

2.1. Study Area and Sampling Sites

The study area is located in the central part of Guangxi Province, belonging to the subtropical monsoon climate. The topography in the study area consists typically of mountains, hills, and basins, with altitudes ranging from 250 to 450 m [22]. The study area is characterized by mild winters and hot summers, with low and high rainfall amounts, respectively. The annual average temperature in the entire Province varies between 16.5 and 23.1 °C. The average annual rainfall reaches 1304.2 mm, and average annual evapotranspiration reaches 639 mm, with an average relative humidity of 79%. Most areas have a warm climate and heavy rainfall, as well as dry and wet weather without significant seasonal variations [22]. The major soil types have been identified as Ferric Acrisols following the
World Reference Base (WRB) for Soil Resources in the study areas [23]. Ferric Acrisols form on old landscapes that have an undulating topography and a humid tropical climate [12]. Ferric Acrisols are generally characterized as soils that have gone through deep and intensive weathering, and have a residual accumulation of resistant minerals (e.g., quartz) and subsequently formed clay minerals (e.g., kaolinite and gibbsite) [12].

A total of 15 pieces of surface soil samples (0-20 cm) were collected. Each soil sample, of about 2 kg, was collected, stored in polyethylene bags, air-dried for about 5 days, and sieving through 2 mm nylon sieves [3]. During sieving, FMNs larger than 2 mm were manually collected, washed with deionized (DI) water (18.25 MΩ), and dried. They were mainly elliptical. More details about the FMNs sample locations are shown in Table S1 and sampling methods correspond to those reported by Ji et al. [3].

2.2. X-ray Powder Diffraction Data

The mineral composition of FMNs in soil is complex, and it is difficult to identify by optical microscopy. X-ray powder diffraction can more easily provide an insight to understand the mineral composition.

X-ray powder diffraction was performed in the Key Laboratory of Surficial Geochemistry, Ministry of Education, Nanjing University. The bulk soil samples were first washed with deionized water and dried at room temperature, then ground to a particle size less than 200 µm, oven-dried at 105 °C, and cooled to room temperature [17]. The sample pieces were made using the back pressure method. The aluminum sample frame was placed on a flat ground glass plate, then the prepared FMNs powder was placed into the sample frame and pressed vertically and evenly. The downward side was the test surface. The X-ray diffractometer (BRUKER-D2 PHASER) operated at 24 ± 2° C. The X-ray anode consisted of Cu, with a receiving gap of 0.03 mm, operating with a current of 10 mA, voltage of 30 KV, and scanning speed of 2°/min. In addition, the scanning range was 3°~80°. XRD patterns were analyzed using Jade 6.0 software using the Rietveld full-pattern fitting method.

2.3. Chemical Analysis

The SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, K₂O, and P₂O₅ concentrations in FMNs samples were determined using X-ray fluorescence spectroscopy analysis (XRF, Thermo Fisher Scientific ARL9900, Waltham, MA, USA), while Mn concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Fisher Scientific iCAP7400, America) after extraction with HCl–HNO₃–HClO₄–HF [17]. The accuracy of the analytical methods was assessed based on standard reference materials (GSS17, GSS22, GSS25, and GSS27), while the log deviation (ΔlgC) between the observed mean value of each standard sample and the recommended value (Cs) of an element in that sample reported by the state was calculated separately [10,22]. During the testing process, the random-based cryptographic sample insertion technique, national standards of substances, the relative double difference (RD/%), and logarithmic deviation (ΔlgC) of the data were used to assess the accuracy of the repeated results obtained using analytical methods. RD/% and ΔlgC values were calculated using the following equations:

\[ RD(\%) = 1/n \sum |C_1 - C_2| / [(C_1 + C_2)/2] \times 100\% \]  (1)

where \( C_1 \) and \( C_2 \) denote the test values of the basic analysis and duplicate samples, respectively.

\[ \Delta \lg C = |\lg C_i - \lg C_s| \]  (2)

where \( C_i \) denotes the value of a certain test of a sample; \( C_s \) denotes the standard sample value.

The detection limit, detection method, and accuracy results of each soil element oxide are reported in Table S2. In addition, the RD/% and ΔlgC values were below 5% and 0.05, respectively. Therefore, the detection limits and accuracies of the corresponding methods and test data met the relevant technical requirements for different soil elements.
3. Results and Discussion
3.1. Concentrations of FMNs in Soils

The concentrations of FMNs are reported in Table 1. According to the obtained results, the order of the oxide element contents in FMNs was as follows: Fe₂O₃ (30.06%) > SiO₂ (19.72%) > Al₂O₃ (17.93%) > TiO₂ (0.96%) > P₂O₅ (0.78%) > MnO (0.64%) > MgO (0.21%) > CaO (0.13%) > K₂O (0.12%) > Na₂O (0.05%). The results showed that the main elemental compositions of soils were Al₂O₃, SiO₂, Fe₂O₃, and MnO₂. In addition, the results revealed relatively obvious spatial differences in the chemical composition of FMNs in soils. On the other hand, the order of the average abundance of oxide elements in FMNs in the main soils of non-karst areas in China was as follows: SiO₂ > Fe₂O₃ > Al₂O₃ > MnO₂ > MgO > CaO > TiO₂ > K₂O > Na₂O > P₂O₅ [24]. The average elemental abundance of 1–2 mm nodules follow the order of SiO₂ > Fe₂O₃ > Al₂O₃ > MnO > K₂O > TiO₂ > MgO > Na₂O > P₂O₅ > CaO in a southern Indiana loess [4]. There were some differences in the composition content of Fe and Mn nodules in the soils of karst and non-karst areas, and the Fe and Mn contents were relatively higher in karst areas, while the Si content was higher in non-karst areas [24], which is mainly related to the parent rock. The results of the current study revealed that the average Mn/Fe value was 0.019 (Table 1). The Mn/Fe ratio is an important indicator of the basic chemical properties of FMNs [1]. The average Mn/Fe value Al/Si is 1.03 (Table 1).

Table 1. Concentrations of major elements in the FMNs (n = 15).

| Item             | Al₂O₃ (%) | SiO₂ (%) | Fe₂O₃ (%) | MnO₂ (%) | K₂O (%) | Na₂O (%) | CaO (%) | MgO (%) | P₂O₅ (%) | TiO₂ (%) | Mn/Fe | Al/Si |
|------------------|-----------|----------|-----------|----------|---------|----------|---------|---------|----------|----------|-------|-------|
| Minimum value    | 16.06     | 13.47    | 26.33     | 0.27     | 0.07    | 0.04     | 0.10    | 0.17    | 0.60     | 0.67     | 0.008 | 1.35  |
| Median           | 17.7      | 17.46    | 30.96     | 0.62     | 0.12    | 0.05     | 0.13    | 0.22    | 0.76     | 0.89    | 0.017 | 1.15  |
| Maximum value    | 19.89     | 27.93    | 32.37     | 1.29     | 0.19    | 0.05     | 0.21    | 0.26    | 0.97     | 1.63    | 0.037 | 0.81  |
| Mean             | 17.93     | 19.72    | 30.06     | 0.64     | 0.12    | 0.05     | 0.13    | 0.21    | 0.78     | 0.96    | 0.019 | 1.03  |
| Standard deviation | 1.23   | 5.13     | 2.29      | 0.32     | 0.04    | 0.002    | 0.04    | 0.028   | 0.13     | 0.29    | 0.009 | 0.27  |
| Coefficient of variation | 0.07  | 0.26     | 0.08      | 0.50     | 0.33    | 0.04     | 0.31    | 0.13    | 0.17     | 0.30    | 2.111 | 0.30  |

Concentrations of major elements in the FMNs in karst areas and non-karst areas are shown in Table S3. Publicly available research data show that there are some differences in the composition of the main elements of FMNs in karst and non-karst areas; the main difference is that the contents of aluminum (>9%) and iron elements (>19%) in FMNs in karst areas is relatively high, the content of silicon elements is relatively low (<11%), and there is no significant difference in the content of other elements such as manganese and calcium elements (Table S3). Due to the special soil-forming parent material and special climatic conditions leading to a large loss of other elements and a large accumulation of iron and aluminum, a portion of the other elements will be lost. Both the A-CN-K diagram and correlation between Fe₂O₃ and Al₂O₃ contents in the samples from profiles in karst areas illustrates the same perspectives [12]. FMNs in karst areas tend to represent the product of the late stage of weathering but not in other non-karst areas.

3.2. Mineral Composition and Environmental Importance of Soil FMNs

The elemental composition of FMNs is closely related to their mineral characteristics. Indeed, contrary to FMNs with low elemental contents, those with high elemental contents are relatively able to form independent minerals and participate in the composition of other minerals in a homogeneous manner. The X-ray diffraction results revealed complex FMNs in bulk soils of the study area, consisting mainly of quartz (SiO₂), goethite (α-FeOOH), clinoclore ([Mg, Fe]₄₋₅Al₁₋₅[Si₂₋₅Al₃₋₅O₁₀]·(OH)₂), iillite ([K₀₋₅Al₁₋₅R₂₋₅Si₂₋₅Al₃₋₅O₁₀](OH)₂), kaolinite (2SiO₂·Al₂O₃·2H₂O), boehmite (Al₂O₃·H₂O), albite (Na₂O·Al₂O₃·6SiO₂), microcline (K[AlSi₃O₈]), liithiophorite [LiAl₂MnO₃(OH)₆], and hematite (α-Fe₂O₃) (Figure 1). Minerals in FMNs can be classified into primary and secondary minerals according to their sources. Primary minerals are derived directly from the
parent rock, while secondary minerals are formed through the decomposition and transformation of primary minerals [2,17,18]. The results demonstrated spatial differences in the mineral composition of FMNs in bulk soils. In addition, the main mineral components of typical FMNs included quartz, goethite, hematite, chloride, layered silicate minerals (mica, potassium feldspar, and illite), as well as some sodium manganese minerals and lithium anhydrite (Table 2). On the other hand, quartz, clinochlore, albite, and microcline were the primary minerals, while goethite, illite, kaolinite, boehmite, lithiophorite, and hematite were the secondary minerals in the study area.

![X-ray pattern of the studied FMNs from the study area. (A)](image)

**Figure 1.** An X-ray pattern of the studied FMNs from the study area. Qtz-quartz; Gth-goethite; Clc-clinochlore; Ill-illite; Kln-kaolinite; Bhm-boehmite; Ab-albite; Mc-microcline; Lit-lithiophorite; Hem-hematite.

Quartz (SiO$_2$) was found in almost all FMNs in the collected samples (Table 2), and is one of the main abundant rock-forming minerals characterized by excellent hardness and weatherability, while the main component was silica. Quartz (SiO$_2$) was present mainly in the mineral fraction of FMNs with two major reflections at $\sim$3.34 and $\sim$4.26 Å (Figure 1). Moreover, quartz was the most common mineral in FMNs and tended to be the primary mineral, reflecting minerals that were not completely weathered during the parent rock weathering process [6]. Quartz minerals can be formed during the nodule formation process [3–5,16]. On the other hand, goethite (α-FeOOH) and hematite (α-Fe$_2$O$_3$) tended to be the secondary minerals formed through the decomposition and transformation of the primary minerals [2,15]. In addition, Fe and Mn oxides, oxyhydroxides, and hydroxides were the most basic components of FMNs nodules. Several studies have pointed out that most FMNs can be developed from Fe and Mn oxides [3,6,16]. The mineral composition of soil Fe and Mn oxides and FMNs are reported in Table 3. According to the obtained results, about five types of manganese oxides and four types of Fe oxides were observed in soils and FMNs, respectively. In addition, goethite (α-FeOOH) and hematite (Fe$_2$O$_3$) were abundant Fe oxides in soils and FMNs (Table 3). Both goethite and hematite were observed in different areas with different climatic zones (Table 2), suggesting that these elements are relatively stable under different climatic conditions.

Lithiophorite [LiAl$_2$Mn$_3$O$_8$(OH)$_6$] is a common soil mineral, observed mainly in acidic and neutral soils, which is often distributed in sub-surface and core soil. The results revealed that this mineral is abundant in FMNs (Table 3). The formation of minerals containing Mn in soils is directly related to the soil Mn contents. That Mn contents in FMNs of the soil...
were generally greater than 1% was reported by Suda et al. [1]. Whereas the results of the current study showed that elemental Mn contents in FMNs ranged from 0.27 to 1.29%, with an average value of 0.64% (Table 1). The study area is located in the subtropical zone, with strong weathering and leaching. Indeed, since the basic ions, including Ca, Mg, K, and Na, were almost completely leached (Table 1) and the ionic strength of the soil solution was weak, the Mn mineral was formed into a single phase [3,11,12]. Moreover, the different types and contents of Mn minerals contained in different FMNs are obviously due to their different material characteristics, environmental conditions, and geochemical processes [25]. Lithiophorite [LiAl$_2$Mn$_3$O$_6$(OH)$_6$] was observed mainly in the heavy mineral fraction of FMNs with two major reflections at ~2.37 (overlapping with pyrochroite) and ~9.21 Å (Figure 1). Manganese-bearing minerals have an important influence on the adsorption of heavy metals in soils, including Cd, Cu, Ni, Pb, and Zn, while Fe-bearing minerals have an important influence on the adsorption of As and Cr [3–5,17,18]. On the other hand, the results revealed some differences in the mineral composition of FMNs in different soil types (Table 2). Some scholars have systematically studied the Mn minerals type of nodules in different soil types in China and have demonstrated high crystallinity of Mn minerals and single mineral type in the red soils, particularly for lithiophorite, while the brown soil had manganese minerals with different crystallinity and richer mineral types, including calomel, hard lithium-manganese-ore, and black zinc-manganese ore. In addition, the crystallinity and mineral types of manganese minerals in yellow-brown soils showed similar characteristics to those observed in red and brown soils [24,25]. The enhanced humidity and temperature from north to south in China, as well as the acidic soil conditions, promote the formation of single Mn minerals, which is consistent with the results obtained in this study showing the presence of a single Mn mineral in the study area [24]. Previous studies have observed Mn mineral types in soils and FMNs in different areas in China, with the occurrence of lithiophorite and small amounts of hollandite and coronadite in red soils in FMNs in Yizhang and Guiyang in Hunan Province. These findings provide evidence that the adsorption of heavy metals on soil FMNs concern mainly Fe and Mn elements [2,17,26].

Illite (K$_{0.75}$(Al$_{1.75}$R)[Si$_{3.5}$Al$_{0.5}$O$_{10}$(OH)$_2$] tends to be formed by weathering and potassium removal from aluminosilicate minerals, such as feldspar and mica, under slightly low temperature and weakly alkaline conditions. Whereas kaolinite (2SiO$_2$·Al$_2$O$_3$·2H$_2$O) is formed by aluminosilicate minerals, such as feldspar and augite, during the weathering process. Indeed, both illite and kaolinite are clay minerals. These two minerals are observed in FMNs, mainly in temperate maritime, mountainous, and temperate maritime climatic zones [27,28]. However, these two minerals are relatively unstable and can be further evolved under superogenesis conditions. On the other hand, clinochlore (((Mg,Fe)$_{4.75}$Al$_{1.25}$)[Al$_{1.25}$Si$_{2.75}$O$_{10}$(OH)$_8$]) tends to exist in an alkaline environment with low leaching potentials [11]. During the weathering process, the divalent Fe (Fe$^{2+}$) in its brucite-like phase can be easily oxidized, affecting the formation of clinochlore since it can only exist in areas where chemical weathering is inhibited. Boehmite is closely influenced by climatic conditions, particularly in humid tropical zones that are characterized by high temperature and rainfall where lateritic soils are abundant. However, boehmite has been rarely investigated in research studies. The environment in which boehmite is formed indicates a humid and hot climate with strong chemical weathering. Indeed, the gibbsite was investigated in Okinawa city in Japan and Serra do Navio in Brazil (Table 2). Both albite (Na$_2$O·Al$_2$O$_3$·6SiO$_2$) and microcline (K[AlSi$_3$O$_8$]) are feldspar minerals, consisting mainly of aluminosilicate minerals, which are primary minerals with low weathering resistance.
Table 2. Literature review of the mineralogical composition of the FMNs in typical soils.

| Regions                             | Soil Type          | Mineral Type of the FMNs                                      | Climate Features                       | References |
|-------------------------------------|--------------------|----------------------------------------------------------------|----------------------------------------|------------|
| Sicily, Italy                       | Alfisols           | quartz, kaolinite, goethite                                    | Subtropical zone                       | [26]       |
| Southern Indiana, America           | Loess              | quartz, feldspars, muscovite, goethite, plagioclases, mica, rutile. | Subtropical zone                       | [6]        |
| Northern Namibia                    | Luvisol            | birnessite, goethite, hematite, illite, muscovite, lithiophorite, pyrochlore, quartz | Tropical zone                          | [17]       |
| Quzhou City in Zhejiang Province, China | Typic Plinthudult | quartz, muscovite, kaolinite, hematite                          | Subtropical zone                       | [16]       |
| Geneva basin, Western Switzerland   | /                  | quartz (21.88%), plagioclase (5.06%), K-feldspar (1.24%), illite (42.77%), chlorite (4.80%), calcite (0.01%), muscovite + biotite (5.09), kaolinite (0.12%), rutile (0.19%) | Temperate maritime climate zone; highland mountain climate zone | [27]       |
| Carpathian Foothills, Poland        | Albeluvisols       | quartz, feldspars, plagioclases, mica, kaolinite, smectite, mica smectite, mica-vermiculite, mica-vermiculite-smectite, goethite, todorokite, zincite, manganite | Temperate maritime climate zone; highland mountain climate zone | [29]       |
| Eastern Germany                     | Stagnosol          | quartz, chlorite, feldspar, illite, kaolinite, goethite, muscovite, | Temperate maritime climate zone        | [28]       |
| Guiyang in Hunan Province, China    | Hapludult          | lithiophorite                                                  | Subtropical zone                       | [30]       |
| West coast of the Pacific Ocean, south Russian Far East | Udepts          | quartz, ferrosilite, jacobsite, iwakiite, sillimanite, hematite, tephroite, bixbyite | Temperate monsoon climate zone; temperate continental climate zone | [31]       |
| Wuhan, China                        | Alfisol            | ferrihydrite, goethite, lithiophorite                           | Subtropical zone                       | [32]       |
| France                              | Lithosol           | quartz, feldspar, kaolinite, mica, goethite and anatase        | Temperate maritime climate zone        | [33]       |
| Okinawa City, Japan                 | /                  | kaolinite, birnessite, lithiophorite, gibbsite and goethite    | Subtropical maritime climate zone      | [34]       |
| Serra do Navio, northern Brazil     | Lateritic soil     | kaolinite, gibbsite, goethite, hematite, quartz and lithiophorite | Tropical monsoon climate zone          | [35]       |
| Longan county in Guangxi, China     | Lateritic soil     | quartz, goethite, cronstedtite, illite, calcite                | Subtropical monsoon climate zone       | [8]        |
| Nanning in Guangxi, China           | Lateritic soil     | quartz, goethite, clinochlore, illite, kaolinite, boehmite, albite, microcline, lithiophorite and hematite | Subtropical monsoon climate zone       | This study |
Table 3. The mineral composition of Fe and Mn oxides (oxyhydroxides) in FMNs.

| Types          | Minerals          | Chemical Composition | References          | Possible Conditions                                                                 |
|---------------|-------------------|----------------------|---------------------|-------------------------------------------------------------------------------------|
| Manganese oxides | Birnessite        | Mn$_7$O$_{13}$·5H$_2$O | [34,36]             | A manganese-bearing mineral common in soils, especially in acidic to neutral subsurface soil layers and FMNs |
|                | Vernadite         | δ-MnO$_2$            | [32]                | A manganese-bearing mineral commonly found in FMNs                                    |
|                | Lithiophorite     | (Al,Li)MnO$_2$(OH)$_2$ | [32,36,37]         | A manganese-bearing mineral common in soils, especially in acidic to neutral subsurface and core soil layers and FMNs |
| Iron oxides    | Manganite         | γ-MnOOH              | [29]                | occasionally found in FMNs                                                          |
|                | Coronadite        | Pb$_2$Mn$_8$O$_{16}$ | [22]                | occasionally found in FMNs                                                          |
|                | Ferrihydrite      | Fe$_5$(O$_4$H)$_3$   | [32]                | occasionally found in soil and FMNs                                                  |
|                | Goethite          | α-FeOOH              | [32,34]             | occasionally found in soil and FMNs                                                  |
|                | Hematite          | α-Fe$_2$O$_3$        | [36]                | occasionally found in soil and FMNs                                                  |
|                | Lepidocrocite     | γ-FeOOH              | [36]                | occasionally found in soil and FMNs                                                  |

4. Conclusions

The results of the present study showed complex mineral compositions of FMNs in the karst areas, in Guangxi Province, Southwestern China. The results showed that Fe$_2$O$_3$ (30.06%), SiO$_2$ (19.72%), Al$_2$O$_3$ (17.93%), TiO$_2$ (0.96%), P$_2$O$_5$ (0.78%), and MnO$_2$ (0.64%) were the main elemental composition, while four alkaline oxides K$_2$O, Na$_2$O, CaO, and MgO were less than 0.5% in soil FMNs. Alkaline cations are easily lost during weathering of parent rocks into soil, which will experience further loss during further evolution of the soil to form the FMNs. The contents of aluminum (>9%) and iron elements (>19%) in FMNs in karst areas are higher than that of no-karst areas, the content of silicon elements (<11%) is lower than that of non-karst areas. In addition, 10 mineral types were identified in this study, namely quartz, goethite, clinochlore, illite, kaolinite, boehmite, albite, microcline, lithiophorite, and hematite. Quartz, clinochlore, albite, and microcline were primary minerals, while goethite, illite, kaolinite, boehmite, lithiophorite, and hematite were secondary minerals. There were no obvious differences in the mineral composition of soil FMNs in the study area compared with those observed in non-karst areas worldwide. There were some differences in the mineral composition of Fe–Mn nodules in soils of karst areas and the high and low content of Fe–Mn nodule elements in non-karst areas, specifically Fe and Mn contents were relatively higher in karst areas, while the Si content was higher in non-karst areas. However, there were no obvious differences in the mineral composition of soil FMNs in the study area compared with those observed in non-karst areas worldwide. The study area in karst regions represented tropical and subtropical climatic conditions, with abundant rainfall and high temperature. These climatic conditions are, in fact, very conducive to the weathering of minerals, resulting in several types of secondary minerals. However, some minerals were not completely weathered, indicating a high formation rate of soil FMNs in the study area, and thus were embedded. In addition, the results suggested relatively stable environmental conditions following the formation of soil FMNs, preserving some primary minerals. In contrast, the results indicated unstable secondary minerals in soil FMNs. Under different environmental conditions, minerals in FMNs can evolve into more stable mineral forms. The present study on the mineral composition in soil FMNs can be useful in understanding the formation process of FMNs, which can be a relatively rapid formation process under warm and rainy conditions.


Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su141912457/s1, Table S1: GPS coordinates of sampling sites in this study; Table S2: Detection limit, detection method, accuracy and precision of each oxide; Table S3: Concentrations of major elements in the FMNs in karst areas and no-karst areas. References [6,8,12,17,24,32] are cited in the supplementary materials.

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