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TECHNICAL NOTE

Occurrence Modes of Niobium in Kaolin Clay From Guizhou, China

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Abstract

Niobium in kaolin clay from the Late Permian sequences was reported in the range of several hundreds of micrograms per gram and was considered as a potential resource for its high concentrations and large areal distribution. Ti-bearing minerals associated with kaolin clay were identified as the main host phase for niobium in some case studies. However, the correlation between the concentration of niobium and titanium is poor, and the types of Ti-bearing minerals and modes of occurrence of niobium are not clear. Typical kaolin clay samples from the Late Permian sequences from southwest China were characterized, and the final products derived from kaolin clay sample were investigated using XRF, ICP-MS, XRD, SEM, and TEM (EDS). The results reveal that there were three types of TiO_2 mineral phases in the clay samples: (a) massive TiO_2 minerals and (b) aggregates of nano TiO_2 minerals did not contain niobium while (c) granular TiO_2 minerals were the source of niobium from the EDS analysis. The granular TiO_2 minerals included anatase and rutile, both of which were the sources of niobium in kaolin clay in the current study. The findings are of great theoretical implication for source and origin study of Ti-bearing minerals and guidance for separation and recovery of niobium from kaolin clay.

Keywords Niobium occurrence · Titania · Morphology · Kaolin clay

1 Introduction

Niobium (Nb) is a strategic metal with extensive uses in many fields, and the demand for Nb in the world market has been increasing for the past decades due to its application in steel and alloy industries [1, 2]. Pyrochlore, columbite, fersmite, and fergusonite occur in nature as common niobium-bearing minerals [3]. Magmatic Nb-Ta (tantalum)-Sc (scandium) deposits and sedimentary Nb-Ta deposits are the two major categories for geological and geogenic classification [4]. The sedimentary Nb-Ta deposits include two sub-categories, i.e., Nb-P (phosphorus)-Ti (titanium) laterites and bauxites and Sn (stannum)-Ta-Nb placer deposits. Worldwide, more than 95% of niobium ore reserves were evaluated in Brazil and Canada. The unbalanced distribution of niobium resources and the increasing industrial demand for niobium have encouraged the exploitation and processing of new niobium resources.

In China, Nb-containing clay from the Late Permian sequences was reported as a potential resource for its high concentrations and large areal distribution [5, 6]. The Late Permian sequences in southwest China (including western Guizhou Province, eastern Yunnan Province, and southern Sichuan Province) are referred to as the Xuanwei Formation, and the lower part of this sequence is mainly composed of kaolinitic clay rocks [7, 8]. The kaolinitic clay rocks from Xuanwei Formation were reported as new polymetallic resources of niobium, rare earth elements, zirconium, gallium, etc., for their high concentrations [5, 8–10]. The content of Nb in the kaolinitic clay rocks is mainly in the range of 200–600 μg/g and is generally higher than that of weathered crust Nb deposits according to the Chinese Geology Mineral Industry Standard [6], which defines that the content of Nb_2O_5 for exploration should be no less than 160 to 200 μg/g.

The kaolinitic clay from the Xuanwei Formation was known to have a sedimentary environment [7]. However, Nb found in the kaolinitic clay was considered as a new type of

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resource instead of a common sedimentary Nb-Ta deposit (neither a Nb-P-Ti laterite and bauxite nor a Sn-Ta-Nb placer deposit). Because the Nb resource was newly discovered, modes of occurrences of Nb have not been deeply understood. Nb-ilmenite was found in the samples from the Xuanwei Formation and was considered as one of the Nb-bearing mineral phases [11]. However, Nb-ilmenite occurred as fine dispersed grains and was rarely observed under SEM-EDS [11]. That means Nb-ilmenite has no sufficient content for us to interpret the high concentrations of Nb in all samples. Ti-bearing minerals were identified as the main host phase for Nb in the clay samples from Egypt [12]. There was no correlation between the concentrations of Nb and Ti from the different clay or host rock samples [13]. Therefore, some researchers assumed that Nb was inferred to be absorbed by clay minerals [5, 11].

The aim of the current work is to depict the modes of occurrences of Nb and to explain the relationship between Nb and Ti in the kaolinitic clay from Xuanwei Formation. The origin of Ti-bearing minerals in kaolinitic clay was also discussed.

2 Materials and Methods

2.1 Sample Collection and Pretreatment

Kaolin clay samples in the bottom part of the Xuanwei Formation were collected from Weining County, Guizhou, China. Three typical kaolin samples representing low titanium (L-Ti), mid titanium (M-Ti), and high titanium (H-Ti) were characterized to investigate the morphology, main and trace elemental composition, and mineral composition in the clay. All samples were dried, ground, and homogenized for examining experiments.

Contents of titanium and niobium in the M-Ti sample were close to the average of the contents of titanium and niobium in the kaolin clay of the whole Xuanwei Formation; thus, it was selected on behalf of the Xuanwei Formation kaolin clay for further study on modes of niobium. The M-Ti samples are typical niobium-bearing kaolin clays in the Xuanwei Formation, and they have been reported for enrichment of Nb and Ti by removing Al and Si in the previous work [6]. As reported before, the final product after removing Al and Si by acid and alkali contains more titanium and is easier to investigate and characterize [6]. In this study, two different series of the final products derived from the M-Ti sample were used to investigate the morphology of titaniferous minerals and the relationship of Ti and Nb, i.e., the final product obtained from clay calcined at 850 °C prior to acid-alkali treatment and the final product obtained from clay calcined at 600 °C prior to acid-alkali treatment. The final product obtained from clay calcined at 850 °C prior to acid-alkali treatment enriched TiO_2 as high as 80.5%, and in this study it was used to investigate the morphology of titaniferous minerals inside. Meanwhile, in view of the phase transformation of titania [14], the M-Ti sample was calcined at 600 °C prior to acid-alkali leaching, and under the above conditions, the final product can reserve the initial species of titania. Therefore, the final product obtained from clay calcined at 600 °C prior to acid-alkali treatment was used to identify of titania minerals.

2.2 Characterization and Analytical Techniques

The main chemical compositions and trace element concentrations of the kaolin clay samples were determined using XRF (PANalytical PW2424) and ICP-MS (Perkin Elmer Elan 9000), respectively [6]. XRF analysis was determined by melting method in conjunction with a loss-on-ignition at 1000 °C, and the lower limit of each datum from XRF is 0.01%. In terms of ICP-MS determination, each sample was added to a lithium metaborate/lithium tetraborate flux, mixed well, and fused in a furnace at 1025 °C. The resulting melt was then cooled and dissolved in an acid mixture containing nitric, hydrochloric, and hydrofluoric acids. Finally, the solution was then analyzed by ICP-MS.

Powder X-ray diffraction measurements were performed using a PANalytical Empyrean diffractometer with Cu Kα radiation. Each sample was prepared by compaction into a silicon sample holder, and a 2θ range between 5° and 70° was scanned. The samples of final products were also observed by an FEI Scios scanning electron microscope (SEM) and a transmission electron microscope (TEM, Tecnai G2 F20 S-TWIN TMP) at an accelerating voltage of 200 kV. Fine sample particles for SEM were dispersed and adhered to a conducting resin and were coated with carbon prior to the microanalysis and observation. For TEM observation, samples were dispersed in alcohol and fixed on a copper supporting net. The techniques employed include high-magnification imaging analysis, high-resolution imaging analysis, energy-dispersive spectrum (EDS) analysis, selected area electron diffraction (SAED) analysis, and Fourier transform structural analysis.

3 Results and Discussion

3.1 Characterization of Nb-Bearing Clay

Tables 1 and 2 show the main chemical compositions and trace element concentrations of the three kaolin clay samples. Al_2O_3, SiO_2, TiO_2, and Fe_2O_3 occurred as the major constituents of all the three samples. TiO_2 in the three samples was determined as 3.67, 8.79, and 11.20%, respectively, and Fe_2O_3 was correspondingly high with increased TiO_2 content. TiO_2 and Fe_2O_3 were reported as common impurities in kaolin

Table 1 Main chemical composition of the samples in this study (wt.%)

Components	Al_2O_3	SiO_2	TiO_2	Fe_2O_3	BaO	CaO	Cr_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SO_3	SrO	LOI	Total
L-Ti	36.44	42.52	3.67	2.55	0.01	0.04	0.01	0.06	0.11	0.01	0.06	0.08	0.01	0.01	14.19	99.77
M-Ti	34.38	39.97	8.79	3.24	0.02	0.03	0.03	0.05	0.10	0.02	0.05	0.09	< 0.01	< 0.01	13.01	99.78
H-Ti	31.14	37.23	11.20	5.72	0.07	0.07	0.04	0.12	0.18	0.02	0.11	0.27	0.13	0.04	12.60	98.94

clays [15]. The content of Al_2O_3, SiO_2, and loss-on-ignition (LOI) decreased with increased TiO_2 content. Other constituents, such as CaO, MgO, Na_2O, and K_2O, were all as minute-quantity impurities. Both niobium and zirconium showed considerable concentrations in the three samples, and they appear to have a good correlation with titanium. Niobium in the clay was equivalent to 551 μg/g, which was much higher than that in the weathered crust Nb deposits in China. The oxides of Nb and Ta should be not less than 160 to 200 μg/g according to industry specifications.

Powder X-ray diffraction was performed (Fig. 1) to identify the mineral composition of the three samples with different titanium contents. Kaolinite (PDF-01-078-2109) and anatase (PDF-01-071-1168) can be matched well in all of the three kaolin samples. Meanwhile, rutile (PDF-01-087-0710) can also be recognized in M-Ti and H-Ti samples for they had high enough titanium. Goethite was judged as one of the Fe-bearing phases in the H-Ti clay sample. This is not contradictory to previous literature [6], in which hematite was identified as an Fe-bearing phase for the sample (M-Ti sample) which was pretreated by calcination at 850 °C. From the main chemical composition data, samples in this study contained high Al/Si molar ratios, compared with other kaolin clays, e.g., Mexican kaolin [16] and Turkish kaolin [17], and it is reasonable that no quartz or other Si polymorphs were found from the XRD patterns. Overall, clay samples in this study consisted of kaolinite, anatase, rutile, goethite, and a very trace quantity of common-impurity minerals [18], if any. In general, the kaolin clay samples in this study had simple mineral compositions, indicative that trace accessory minerals might not be the host phases for niobium since its concentrations in the samples were so high.

3.2 Morphology of Titaniferous Minerals

Although the original clay samples had quite high content of titanium, it is still difficult to identify the correlations between TiO_2 and niobium in the samples. It was proposed that the final product derived from the M-Ti sample after acid-alkali leaching [6] was employed to investigate the categories of Ti-bearing mineral phases, the modes of occurrences of Nb, and the relationship between niobium and Ti-bearing mineral phases. SEM and TEM micrographs as shown in Figs. 2 and 3 reveal that kaolinite was removed in the final product and different crystal morphologies of Ti-bearing minerals could be observed almost anywhere in the microscopic views. The Ti-bearing minerals were actually TiO_2 minerals which could not be identified as anatase or rutile for their particle size was very small. In addition to the TiO_2 minerals, very few inert minerals, e.g., zircon, can also be found.

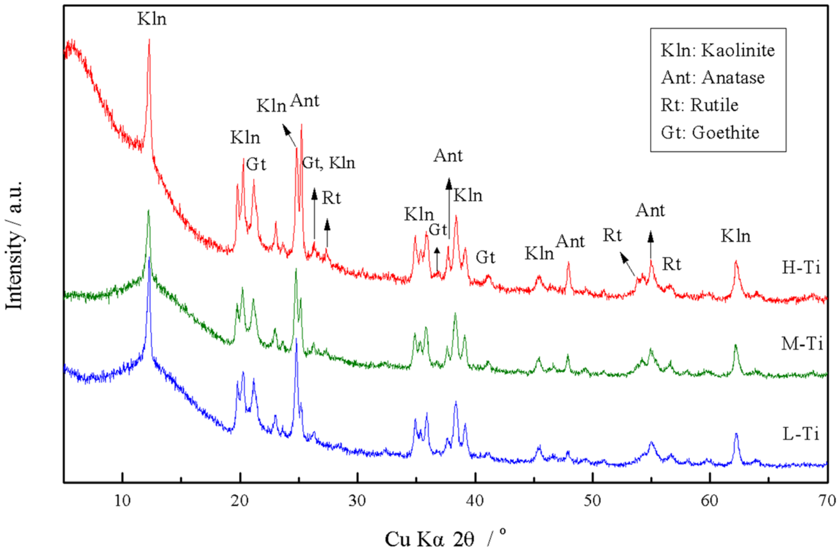
Among the large amount of Ti-bearing minerals in the final product derived from the M-Ti sample, three types of TiO_2 mineral phases were summarized based on the crystal form and size from the TEM analysis (as shown in Fig. 4).

(1) Massive TiO_2 minerals (Fig. 4a). Massive TiO_2 minerals are referred to as relatively large particles with a size of 500–1000 nm or bigger. Under TEM, massive TiO_2 minerals accounted for less than 10% of the Ti-bearing minerals. The massive TiO_2 minerals usually contained very low iron, while niobium was not determined from the EDS analysis. Therefore, massive TiO_2 minerals in this study were not considered as one of the sources of niobium.

Table 2 Trace element concentrations of the samples in this study (μg/g)

Element	Nb	Ta	Zr	Hf	Cr	Ga	Sn	U	Th	V	W	Y	Sc	La-Lu
Lower limits	0.2	0.1	2	0.2	10	0.1	1	0.05	0.05	5	1	0.5	0.1	0.5
L-Ti	206	13.1	1490	38.1	80	54.3	13	8.18	37.5	205	1	61.4	28.7	448.94
M-Ti	491	31.6	3480	93.2	240	98.6	31	15.25	95.8	596	2	38.1	75.3	281.40
H-Ti	551	36.0	3540	98.4	290	102.5	37	20.60	100.5	536	3	198.5	-	1386.9

Fig. 1 XRD patterns of the three kaolin clays with different titanium content



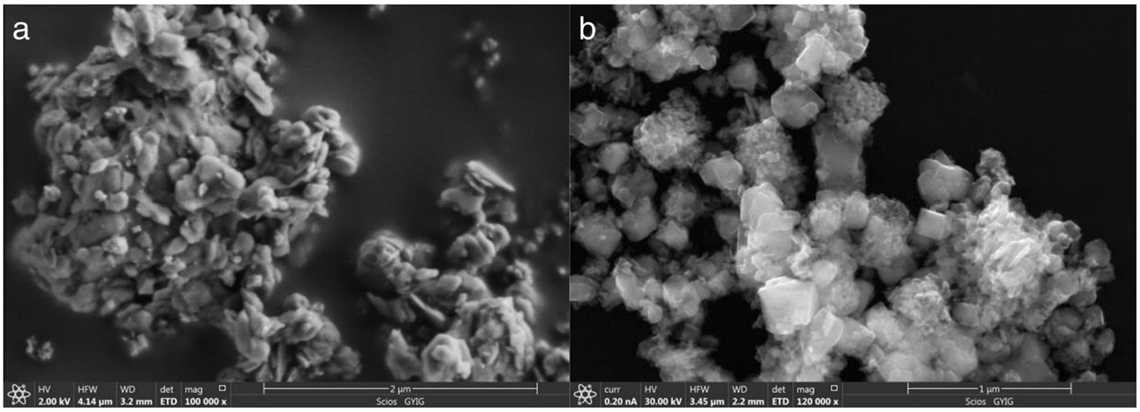


Fig. 2 SEM micrograph of **a** the original clay and **b** its final product derived from clay calcined at 850 °C prior to acid-alkali treatment

(2) Aggregates of nano TiO_2 minerals (Fig. 4b). Small TiO_2 mineral particles with granular or short columnar shape aggregated to form xenomorphic textures. The small TiO_2 particles were nanoscaled (less than 50 nm) and occurred closely together. Therefore, aggregates of nano TiO_2 minerals could be easily mistaken for massive TiO_2 minerals if the magnification times were not high enough. These form of TiO_2 minerals accounted for about 20-30 % in the microscopic views of TEM. There was no niobium peaks determined from the EDS analysis, and aggregates of nano TiO_2 minerals in this study were not considered as one of the sources of niobium. In addition, aggregates of nano TiO_2 minerals contained the highest content of iron of the three TiO_2 forms.

(3) Granular TiO_2 minerals (Fig. 4c). Granular TiO_2 minerals were the dominant form of the Ti-bearing

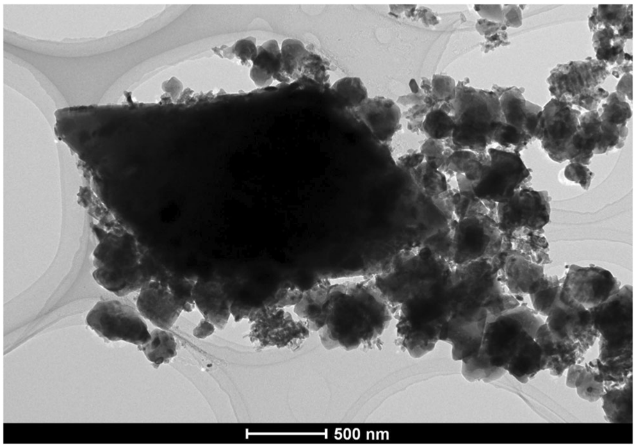


Fig. 3 TEM micrograph of the final product derived from clay calcined at 850 °C prior to acid-alkali treatment

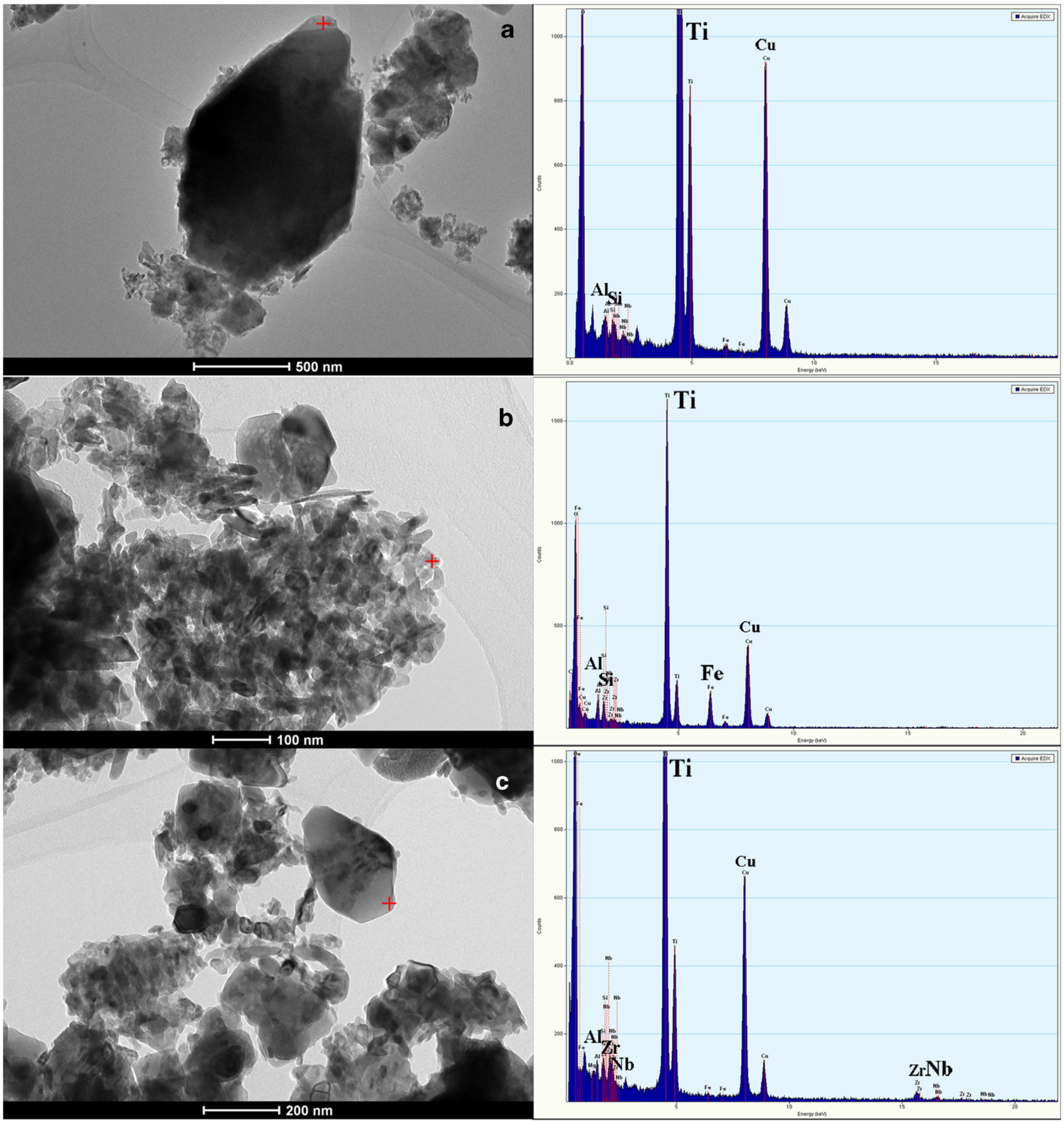


Fig. 4 TEM micrographs and EDS analysis of titaniferous minerals in the final product derived from clay calcined at 850 °C prior to acid-alkali treatment, **a** massive TiO_2 minerals, **b** aggregates of nano TiO_2 minerals, and **c** granular TiO_2 minerals

minerals, accounting for more than 60% under TEM. The granular minerals are round, cubic, short columnar shape, and always having about a 100–300-nm diameter. The niobium and zirconium peaks could be determined by the EDS analysis. It indicates that Nb is in the structure of granular TiO_2 minerals.

The fact that massive TiO_2 minerals and aggregates of nano TiO_2 minerals did not contain Nb inside explained the poor positive correlations between TiO_2 and Nb in the clay samples, especially for samples with high TiO_2 and low Nb.

3.3 Identification of Nb-Bearing Titania Minerals

Rutile is suggested as the major Ti-bearing mineral that retains the high field strength elements (such as Nb and Ta) during magma partial melting [19, 20] because rutile can incorporate Fe, Nb, Ta, etc., as isomorphic impurities. However, anatase has been widely considered as the dominant Ti-bearing phase and an essential constituent in sedimentary kaolin deposits [12, 21]. Anatase contents in clay samples containing ~ 1.5 wt.% TiO_2 with different colors from a Georgia kaolin deposit ranged from half to nearly all the TiO_2 [21], and anatase also occurred as the principal Ti-bearing mineral in sedimentary kaolin

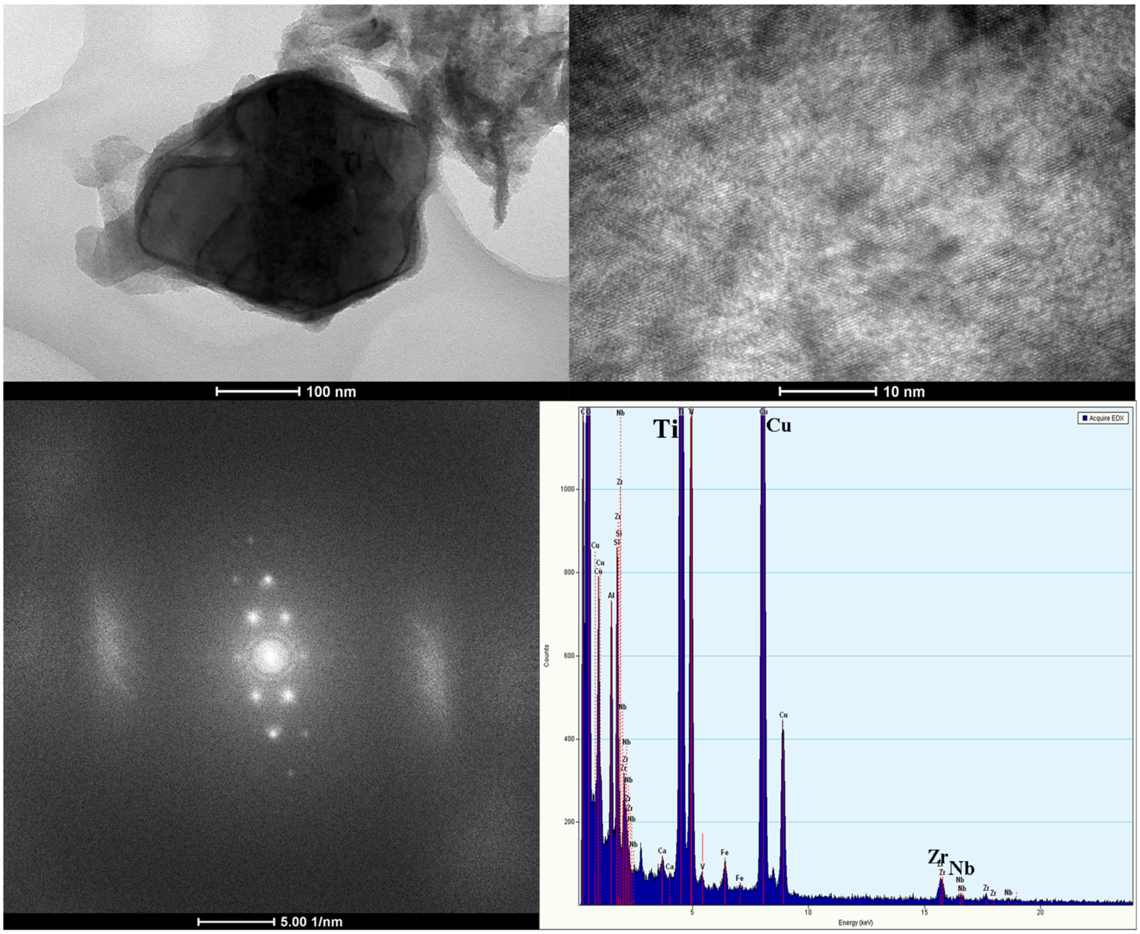


Fig. 5 TEM micrographs and EDX analysis of anatase in the final product derived from clay calcined at 600 °C prior to acid-alkali treatment

deposits of Egypt [12]. Most of trace elements such chromium, niobium, and zirconium in the clay fractions were considered in the anatase structure, which included fine-grained or rounded crystals [12].

In the current study, different morphologies of Ti-bearing minerals were observed in the final product derived from the M-Ti kaolin clay sample, and granular TiO_2 minerals were considered as the source of Nb. Since the modes of occurrence of Nb had involvement with the morphologies of titania minerals, the species of Nb-bearing TiO_2 minerals were further identified by TEM and SAED (selected area electron diffraction) to find the relationship between Nb and Ti in the kaolinitic clay. From the 7 individual granular particles of TiO_2 minerals, three of them were identified as rutile and four of them were anatase. The results show that the granular TiO_2 minerals included anatase (Fig. 5) and rutile (Fig. 6). That means both anatase and rutile were confirmed as the sources of Nb in the kaolin clay used in the current study. According to the TEM analysis, the amount of anatase phase in the samples was higher than that of rutile, which was in agreement with the results of XRD.

The findings will be of use for confirming the source of Nb and formation of Ti-bearing minerals during the natural weathering process to form sedimentary kaolin deposits. Rutile or anatase allows Nb to be more easily accommodated in its structure, which has been discussed elsewhere [12, 22]. It is known that rutile in sedimentary clay is as residuals derived from a parent rock while anatase in sedimentary clay is newly formed during the weathering process. Within the kaolin sample, rutile occurs in the sand fractions and anatase occurs as uniform very fine-grained and rounded crystals [12]. Since anatase and rutile were formed in different geological environments, Nb in the clay samples of this study would have different sources. The findings are also instructive for utilization of Nb resource when the beneficiation process was used to separate Nb-bearing titania minerals if possible.

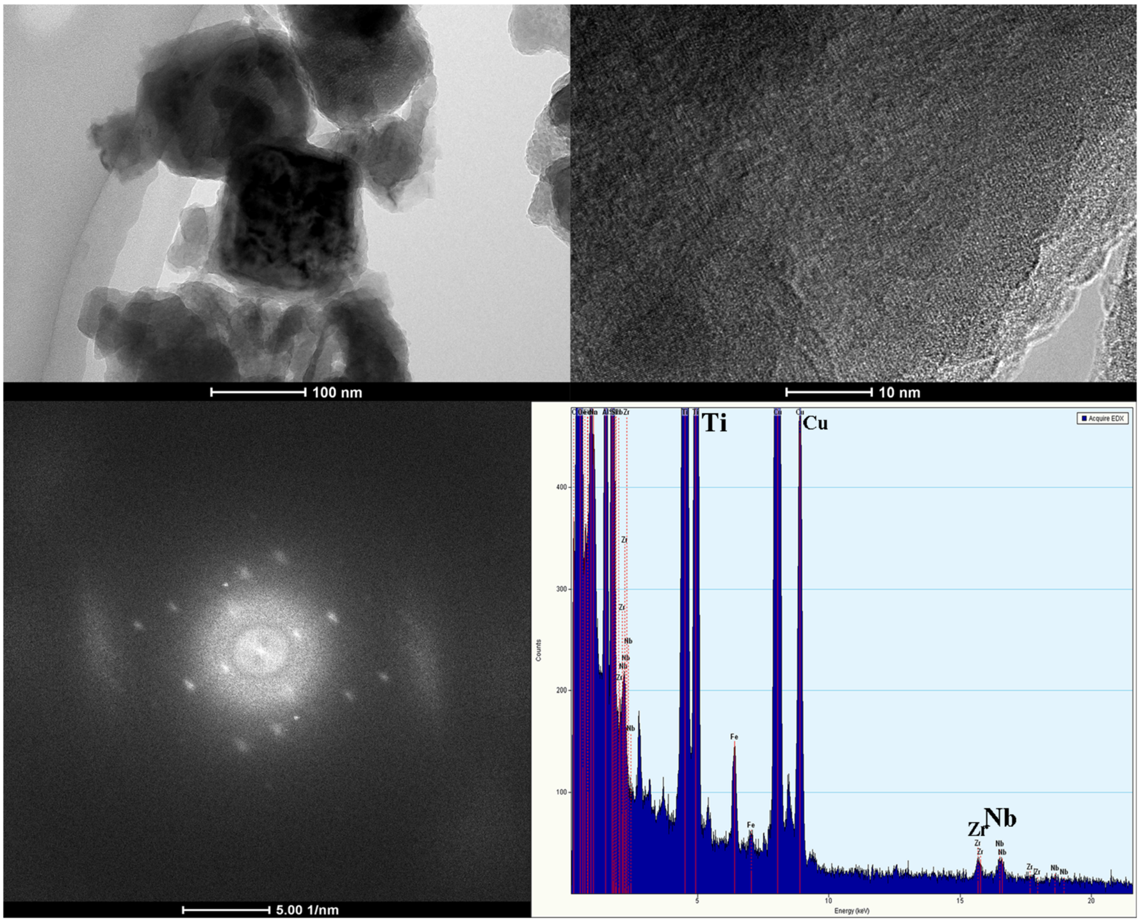


Fig. 6 TEM micrographs and EDX analysis of rutile in final product derived from clay calcined at 600 °C prior to acid-alkali treatment

4 Conclusions

Clay samples with different titanium contents from the Xuanwei Formation, the Late Permian sequences from Guizhou, China, were characterized, and Al_2O_3, SiO_2, TiO_2, and Fe_2O_3 were the major constituents. Niobium in the kaolin clays was in the range of several hundreds of micrograms per gram. Three types of TiO_2 mineral phases in final products derived from one of the kaolin clay samples were grouped: (a) massive TiO_2 minerals that did not contain niobium, (b) aggregates of nano TiO_2 minerals, and (c) granular TiO_2 minerals. The granular TiO_2 minerals included anatase and rutile, and both were confirmed as the sources of niobium in the kaolin clay in the current study. The findings are of great theoretical implication for the source and origin study of Ti minerals and guidance for the separation and recovery of niobium from Ti minerals or kaolin clay.

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Compliance with ethical standards

Conflict of Interest The authors declare that they have no conflict of interest.

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