Surficial weathering of kaolin regolith in a subtropical climate: Implications for supergene pedogenesis and bedrock argillization

Qian Fang\textsuperscript{a,b}, Hanlie Hong\textsuperscript{a,c,d,⁎}, Harald Furnes\textsuperscript{e}, Jon Chorover\textsuperscript{b}, Qing Lu\textsuperscript{f}, Lulu Zhao\textsuperscript{a,b}, Thomas J. Algeo\textsuperscript{c,d,g,⁎⁎}

\textsuperscript{a} School of Earth Sciences, China University of Geosciences, Wuhan 430074, China
\textsuperscript{b} Department of Soil, Water and Environmental Science, University of Arizona, Tucson, AZ 85721, USA
\textsuperscript{c} State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, China
\textsuperscript{d} State Key Laboratory of Geobiology and Environmental Geology, China University of Geosciences, Wuhan 430074, China
\textsuperscript{e} Department of Earth Science, Centre for Geobiology, University of Bergen, Allegt. 41, 5007 Bergen, Norway
\textsuperscript{f} Center for Exploration of Earth Resources of Jiangxi Province, Nanchang 330000, China
\textsuperscript{g} Department of Geology, University of Cincinnati, Cincinnati, OH 45221-0013, USA

\textbf{A R T I C L E   I N F O}

Handling Editor: M. Vepraskas
Keywords: Regolith, Chemical weathering, Chemical gradient, Clay mineral, Kaolinite

\textbf{A B S T R A C T}

Regolith, or in situ weathered material overlying bedrock, develops through pedogenic processes such as clay-mineral formation ("argillization"). Research on products of argillization, such as kaolin, is commonly focused on its economic value rather than on an integrated understanding of the pedological, mineralogic, and geochemical processes taking place in the regolith. Here, we analyzed three kaolin-regolith drillholes from a subtropical climate zone in southern China using X-ray diffraction (XRD), major and trace element analyses, H and O isotopes, differential thermal-thermogravimetric analysis (DTA-TG), and scanning electron microscopy (SEM). Many kaolinite aggregates within regolith have fan-shaped stacks, a morphology that is closely associated with transformation of muscovite plates. Hypogene indicators such as a shallow level of granite emplacement, representative structural controls on kaolinization, mineral zoning, and hypothermal minerals cannot be observed. Mineral assemblages and morphologies, elemental binary plots (e.g., Zr vs. TiO\textsubscript{2} and P\textsubscript{2}O\textsubscript{5} vs. SO\textsubscript{4}), as well as chemical profiles all show characteristics typical of surficial weathering. The δ\textsuperscript{18}O and δ\textsuperscript{2}H values of the clay fractions range from +16.8 to +18.7‰ and from −70 to −51‰, respectively, suggesting that supergene weathering has played a key role in forming the kaolin regolith. Dominance of kaolinite over halloysite implies a near-surface, freely draining environment. Adopting the underlying weakly altered granite (saprolith) as the parent material, the kaolin regolith exhibits four elemental profile patterns as revealed by mass transfer coefficients: (1) depletion (e.g., Na), (2) depletion-enrichment (e.g., Al), (3) enrichment (e.g., Mn), and (4) biogenic (e.g., Ca). These profiles reflect a combination of chemical, geologic, and biologic processes that are typical of relatively thin, in situ regolith profiles, and that is not necessarily similar to those typically associated with deep (thick) granite weathering profiles. We propose that supergene kaolin regolith is intrinsically more similar to shallow, biologically active residual soil deposits, rather than deeply weathered granite-hosted regoliths.

\textbf{1. Introduction}

Regolith is defined as in situ weathered material overlying bedrock, and it is present to varying degrees across the Earth (Wilford et al., 2016). It represents the entire unconsolidated and secondarily re-cemented cover that overlies relatively intact bedrock, and it is formed by erosion, transport/deposition, and weathering of pre-existing material (Anand and Paine, 2002; Keeling et al., 2003). The regolith is host to many of the resources that maintain our society and living standards. It is also in the upper part of the regolith that our soils are formed; the regolith is thus the host for life and agriculture (Taylor and Eggleton, 2001). The distribution and nature of regolith are controlled by various factors, reflecting long-term interactions among the atmosphere, pedosphere, lithosphere, biosphere and hydrosphere (Brantley and White, 2009; Buss et al., 2017). Regolith develops through a variety of processes such as argillization, i.e., the formation of clay minerals in the

⁎ Correspondence to: H. Hong, School of Earth Sciences, China University of Geosciences, Wuhan 430074, China.
** Correspondence to: T.J. Algeo, Department of Geology, University of Cincinnati, Cincinnati, OH 45221-0013, USA
E-mail addresses: honghl8311@aliyun.com (H. Hong), thomas.algeo@uc.edu (T.J. Algeo).

https://doi.org/10.1016/j.geoderma.2018.09.020
Received 15 July 2018; Received in revised form 5 September 2018; Accepted 9 September 2018
Available online 21 September 2018
0016-7061/ © 2018 Elsevier B.V. All rights reserved.
soil environment (Gilkes et al., 1973), and clay minerals commonly provide insights into the nature of these processes (Dill, 2017; Lopez et al., 2018).

One type of argillization process is kaolinization, which generates the mineral kaolin (Ekosse, 2001; Anand and Paine, 2002; Dill, 2017). Kaolin deposits can be formed in situ by hydrothermal processes during late-stage pluton cooling (hypogene), by (near-)surface weathering reactions (supergene), or by a combination of these processes (Dudoignon et al., 1988; Murray, 1988; Dill et al., 1997; Galán et al., 2016). Hypogene processes play a prominent role in alteration of granitic rocks intruded at relatively shallow depths, and it is commonly associated with high acidity and high temperatures (Marfil et al., 2005). In supergene deposits, chemical weathering is the dominant process of formation of kaolin minerals (e.g., kaolinite, halloysite, and dickite) from a variety of parent rocks (e.g., granite, gneiss, and slate; Chorover and Sposito, 1995; Scott and Bristow, 2002; Keeling, 2015; Hong et al., 2016). With time, regolith composition diverges progressively from that of the parent material owing to the cumulative influences of vegetation, biota, topography, and, in particular, climate (Thanachit et al., 2006; Zhao et al., 2017). In the present study, “kaolin regolith” is defined as a residual kaolin deposit that has undergone substantial chemical leaching and physical weathering processes such as regolith creep/flow and erosion by water (Taylor and Eggleton, 2001).

Kaolin genesis has a direct relation to its industrial applications, with supergene kaolins generally being more concentrated and having higher economic value than hypogene ones (Ekosse, 2001; Njøya et al., 2006; Fernandez-Caliani et al., 2010). As a raw material for chinaware, kaolin has substantial economic value, but its economic significance is broader in that kaolin is found in many products for daily use, including paper coating, ceramics, plastics, rubber, cosmetics, and pharmaceuticals (Zhou and Keeling, 2013; Lu et al., 2016; Pruett, 2016). Relatively systematic work on kaolin argillization has been undertaken in Australia (Gilkes et al., 1973; Anand and Paine, 2002), USA (Schroeder et al., 2004), and Europe (Galán et al., 2016). China represents one of the most important producers of kaolin (especially for ceramics, sanitary ware and porcelain; Wilson, 2004). Indeed, the first use of kaolin in pottery manufacture emerged in Jingdezhen, Jiangxi Province, China over 2000 years ago (Schroeder and Erickson, 2014), and the first mining site for gaoing tu (kaolin clay) was the Gaoling area, located 50 km northeast of Jingdezhen. Despite its cultural importance, only limited research concerning the formation of kaolin regolith particularly related surficial weathering process has been conducted in China.

A detailed study of kaolin deposits in China has the potential to improve our understanding of mineral alteration and elemental migration during supergene processes and kaolin accumulation worldwide. The Chongyi kaolin regolith in Jiangxi Province, southern China, is located in a subtropical climate zone with warm temperatures and high rainfall, contributing to its intensely weathered condition. Here, we investigate the Chongyi kaolin regolith using an integrated approach based on XRD, SEM, XRF, ICP-MS, DTA-TG, and H and O isotopic analyses. The goals of this study were to: (1) systematically characterize the kaolin regolith using a variety of mineralogic and geochemical techniques; (2) gain insights into the geochemical behavior of major and trace elements during supergene kaolin argillization; (3) determine the genetic relationships between kaolin regolith and the typical residual soil deposit; and (4) propose a model for kaolin argillization in Earth’s surface environments.

2. Materials and methods

2.1. Study location and climatic setting

The Chongyi kaolin regolith is located in Chongyi County, southwestern Jiangxi Province, southern China (Fig. 1). The landscape consists of low mountains and hilly terrane. Within Chongyi County, elevations fall from northwest (~1000 meters above sea level - masl) to southeast (~500 masl), with rivers thus flowing in a southeasterly direction. The study area is within a subtropical monsoonal climate zone that is characterized by large seasonal variations in air temperature, wind direction, and rainfall, with > 80% of precipitation falling during the period from May to September. Mean annual temperature (MAT) is 17.6 °C, and mean annual precipitation (MAP) is 1600 mm. The Chongyi kaolin regolith is located within the Nanling metallogenic belt, which was generated during the Jurassic-Cretaceous (~200–134 Ma) Yanshanian magmatic event. The Yanshanian event resulted in NE–SW-trending faults and associated pluton emplacement in the study area (Zhou et al., 2006; Wang et al., 2018). The bedrock of the kaolin regolith is a muscovite granite of early Yanshanian age (~200–170 Ma), and the original argillization process may have been driven by magmatic heat.

According to layering of typical regolith profiles by Taylor and Eggleton (2001) and Anand and Paine (2002), the Chongyi regolith can be divided into a lower saprolith layer and an upper pedolith layer (Fig. 2): (1) the saprolith contains saprockor below and saprolite above; and (2) the pedolith contains a plasmic zone, a mottled zone, and an overlying surface layer. The regolith can be further vertically subdivided into four units based on differences in color and lithology (Fig. 2: listed from top to bottom): the surface layer, the mottled kaolin layer, the homogenous kaolin layer, and the saprolith.

2.2. Field sampling

Geological field work included mapping in outcrop and description and sampling of drillcore and drill-cuttings. In each of three drillcores, five samples were collected: one in each regolith layer (surface layer, mottled kaolin, homogenous kaolin, and saprolith) with a second sample taken in the homogenous kaolin layer (the two samples of the homogeneous layer are designated “upper kaolin” and “lower kaolin”). This yielded a total of 15 samples for geochemical analyses (Fig. 2). Clay fractions (< 2 μm) were extracted from 12 samples (all but the three saprolith samples) by conventional sedimentation and centrifugation methods. The < 45 μm fractions were extracted from three kaolin samples (i.e., CY 1–3, CY 2–3, and CY 3–3). The grain-size fraction of 63–600 μm was used for analysis of heavy minerals.

2.3. X-ray diffraction (XRD)

The samples of bulk kaolin (including mottled kaolin and homogeneous kaolin), fine fractions (< 45 μm and < 2 μm), and heavy minerals were mineralogically analyzed by XRD. These samples were pretreated to remove organic matter with 30% H2O2 at 60 °C. Air-dried oriented clay mounts for the < 2 μm fractions were prepared by dispersing the clay slurry onto glass slides. XRD patterns were recorded using a D/max-3B X-ray diffractometer with Cu Kα radiation at 40 kV, 35 mA (resolution ratio = 0.0228; scan rate = 4° 2θ/min; scan range = 3–65°). The formamide test (Churchman et al., 1984) was carried out for the < 2 μm fractions to distinguish halloysite from kaolinite. Bulk-rock mineral contents were determined on randomly oriented powders using reference intensity ratio (RIR) together with the so-called 100% approach (Hillier, 2000). RIR is also known as I/Icor, which represents the ratio of intensities (areas) of specific XRD peaks (mineral: corundum = 1:1). The term 100% approach means that the sum of all mineral phases identified is 100%. Five minerals (muscovite, feldspar, quartz, kaolinite, and gibbsite) that were involved in content calculation have RIR values (refer to corundum 113 peak) of 0.23 (~10.0 Å), 2.07 (~3.20 Å), 0.89 (~4.25 Å), 0.53 (~3.57 Å), 1.91 (~4.85 Å), respectively. Considering this is a semi-quantitative method with a calculation error of 5–10%, we used “——” (not detected), “**” (< 15%), “***” (15–40%), and “****” (> 40%) to describe different mineral contents in order to present more reasonable data (Table S1).
2.4. X-ray fluorescence (XRF)

All collected samples were analyzed for major-, trace-, and rare-earth element (REE) concentrations. Major-element concentrations were measured by XRF spectrometry using a Shimadzu XRF sequential spectrometer. The analytical precision for major-element concentrations was < 1% and the detection limit was 0.01 wt%.

2.5. Inductively coupled plasma-mass spectrometry (ICP-MS)

Trace-element and REE concentrations were determined using an Agilent ICP-MS, with an analytical precision of better than 4% for REEs and 4–10% for other trace elements. Prior to ICP-MS analysis, each sample was leached for ~20 min in 1-N HCl, after which the residue and leachate were separated by continuous centrifugation, and the residue was rinsed with milli-Q water.

2.6. H and O isotopic analyses

The < 2 μm fractions of nine samples (i.e., the six homogenous kaolin plus three mottled kaolin samples) were analyzed for H and O isotope compositions. For analysis of δ¹⁸O values, oxygen in the clay...
fractions was extracted through reaction with BrF5 at 600 °C in a nickel chamber for ~24 h and then converted to CO2 over a graphite furnace (Clauer et al., 2015). For H isotope analysis, the clay fractions were heated at 1500 °C, and the released water was converted to H2 at 900 °C. The converted CO2 and H2 were measured for oxygen and hydrogen isotopes, respectively, using a Finnigan-MAT253 mass spectrometer. Isotopic ratios were reported by δ notation as deviations in per mille versus the international Vienna standard mean ocean water (VSMOW) standard, with reproducibility of ± 0.5‰ for δ18O and ± 1‰ for δ2H values.

2.7. Differential thermal and thermogravimetric analysis (DTA-TG)

Differential thermal-thermogravimetric analysis (DTA-TG) was performed using a Setaram Labsys thermal analyzer, operating under a nitrogen flow of 60 ml/min. Both the bulk kaolin and < 45 μm kaolin samples were selected for DTA-TG analysis. The DTA-TG curves were obtained using 10 mg of powdered sample, heated from room temperature to 1400 °C at rates of 10, 20, 30, or 40 °C min⁻¹. Aluminum was used as a reference material.

2.8. Scanning electronic microscopy (SEM)

Both clay fractions and heavy minerals were selected for SEM analysis. These heavy minerals were hand-picked under binocular microscope after heavy-liquid (solution of lithium heteropolytungstates in water) and magnetic separation of 63-600-μm fractions. An EDS-equipped FEG-SEM (HITACHI-SU8010) was used to observe the micromorphology of the clay minerals and heavy minerals of representative samples and analyze their chemical compositions. These samples were sputter-coated with thin films of platinum prior to analysis. The SEM instrument was operated at a voltage of 10-15 kV, a current of 3-5 nA, and a 15 mm working distance, with observations performed in secondary electron mode.

3. Results

3.1. Mineralogic characteristics

The mineralogic compositions of representative samples are shown in Fig. 3, and data for all samples (including bulk kaolin, < 45 μm fraction, and < 2 μm fraction) are given in Table S1. The mineralogic composition varies with particle size: the clay (< 2 μm) fractions are dominated by kaolinite with subordinate amounts of muscovite, gibbsite, and quartz, whereas bulk kaolin samples contain larger amounts of quartz than kaolinite. Kaolinite is identified by diagnostic narrow peaks at 7.16 Å and 3.58 Å. The non-basal sharp and less intense reflections of quartz than kaolinite. Kaolinite is identified by diagnostic narrow peaks at 7.16 Å and 3.58 Å and triplets at 2.38/2.34/2.30 Å are linked to well-crystallized kaolinite (Fig. 3B, C; Erkoyun and Selin, 1986). Muscovite in hereditary parent granite has concentrations of < 15% in the bulk kaolin samples (Table S1). A ~4.86 Å peak is observed in the XRD patterns of bulk and fine-fraction samples, suggesting the presence of gibbsite (Fig. 3).

3.2. Major- and trace-element compositions

The major-element compositions of the analyzed samples are given in Table S2. The three study sections are similar in their overall chemical compositions. The saprolith is characterized by high SiO2 (mean 66.6%) and low CaO (mean 0.09%) and MnO (mean 0.10%). SiO2 (45.7–75.0%) and Al2O3 (15.0–38.4%) are the major constituents of both the bulk kaolin samples and finer fractions (< 45 μm). Fe2O3 varies from 0.63 to 2.89%, K2O varies from 1.83 to 4.81%, and the remaining major-element oxides show concentrations of < 1%. The finer fractions (< 45 μm) in all three sections show increases in Al2O3 (up to 38.4%) and decreases in SiO2 (mean 46.2%) compared to the bulk kaolin samples (Table S2). The major element concentrations of the samples correspond well to the mineralogic compositions determined by XRD.

Trace elements such as Zn, Zr, and Ba exhibit high concentrations (~100–3600 ppm), V, Ga, Sr, Nb, Ta, and Pb have intermediate concentrations (~10–100 ppm), and Sc, Y, Sn, Th, and U show low concentrations (< 10 ppm). The UCC-normalized trace-element and REE distributions of the kaolin samples show similar features for all samples (Fig. 4), including depletions of many elements (e.g., Zr, Y, Th, and medium-REE Dy) that are usually considered to be resistant to remobilization during weathering, enrichments of some relatively mobile elements (e.g., Ba and Ga), and negative Ce anomalies. These features should be mainly inherited from parent granite rocks, rather than as a result of chemical weathering, because the distribution patterns are similar for weakly weathered saprolith and strongly weathered kaolin samples. These features are typical of trace-element and REE distributions of Mesozoic granitoids in South China (Zhou et al., 2006). Actually it has been widely suggested that chemical weathering can often exert a limited influence on REE distributions of weathered profiles (e.g., Galán et al., 2016; Hong et al., 2016).

3.3. H and O isotopic compositions

Before evaluating the H and O isotopic results, it is necessary to estimate the contributions of impurity minerals to the measured isotopic data. As pointed out by Savin and Lee (1988), the isotope
fractionation factors of weathering-formed (secondary) muscovite and gibbsite are similar to and slightly smaller than those of kaolinite, respectively. However, at least a small part of the muscovite in our samples may be residual primary muscovite from the parent granite, which formed at high crystallization temperatures and has an unknown isotopic composition. As noted before, the halloysite content is negligible and should have contributed little to the measured isotopic data. An empirical approach by Clauer et al. (2015) suggests that the potential influence of contaminant quartz can be disregarded. Assessment of the contributions of impurity minerals to the H isotopic results yields similar conclusions as for O isotopes (cf. Clauer et al., 2015). In conclusion, the minor amounts of impurity minerals in our samples are likely to have only a minor influence, at most, on measured isotopic values.

The $\delta^{18}O$ and $\delta^2H$ values of the clay (< 2 μm) fractions range from +16.8 to +18.7‰ and from −70 to −51‰, respectively (Fig. 5). In a plot of $\delta^{18}O$ vs. $\delta^2H$, the Chongyi kaolin samples mostly lie close to the kaolinite weathering line (representing the isotopic composition of kaolinite in equilibrium with meteoric water at 20°C; Fig. 5).

Supergene kaolin samples of Ramon-Fazouro (Clauer et al., 2015) and Chubut/San Cruz (Cravero et al., 2001) and hypogene samples of Seliz and Kemmliz (Gilg et al., 2003) are plotted for comparison (Fig. 5).

3.4. SEM observations

3.4.1. Kaolin minerals

The kaolin minerals occur either as discrete plates or as composite stacks, and they exhibit one of two morphologies: relatively porous aggregates and well-developed crystals (Fig. 6). The porous aggregates consist of pseudo-hexagonal plates with poorly developed lateral surfaces (010) and (110), yielding irregularly ragged outlines (Fig. 6A). The clay particles range in size from 1 to 5 μm. The second morphology consists of well-developed euhedral pseudo-hexagonal crystals, usually arranged face-to-face in elongated book-like stacks (Fig. 6B). The lateral surfaces (010) and (110) are flat and clearly defined, and the particle sizes are larger, ranging from 3 to 10 μm. Many of the kaolin aggregates are vermiciform or fan-shaped (Fig. 6C–E), and crystal elongation parallel to the c-axis (to 1.5 mm) was retained within the composite stacks. This
The presence of iron and magnesium and the dark color are prismatic, irregular fragments, and sub-rounded to round grains due to magma cooling and crystallization (Wang et al., 2014). Tourmaline is a volatile component of a magmatic system, e.g., during the formation of tourmaline. However, some Ti-oxide minerals are abundant in the heavy-mineral fraction and diverse in chemical weathering but rather about the parent granite rocks (Fig. 4).

Kaolinization in the Chongyi regolith is usually associated with minerals produced through low-temperature chemical weathering, e.g., gibbsite, anatase, and iron-oxides. For example, gibbsite, which is typically found in highly weathered soils/sediments, is generated through alteration of aluminosilicate or aluminous minerals under intense chemical weathering but rather about the parent granite rocks (Fig. 4). Book-like pseudohexagonal kaolinite crystals are commonly due to retention of the original morphology of feldspar crystals (Ekosse, 2001).

3.4.2. Heavy minerals

Ti-oxides are abundant in the heavy-mineral fraction and diverse in their morphology and composition (Fig. 7A, B). The TiO2 content of the bulk samples varies from 0.10 to 0.13 wt%. Ti-oxide minerals always contain a certain amount of niobium (Nb) (Dill, 2017), which can be seen in the EDS spectrum (Fig. 7A) and is an indication (along with an XRD peak at 3.51 Å) that the grain consists of anatase. Some Ti-oxide minerals show indentations and notches along their crystal boundaries, which may reflect intergrowth of rutile with other minerals such as quartz (Fig. 7B). Iron-oxides are rare in the homogenous kaolin layer but relatively abundant in the mottled kaolin layer. Altered magnetite is present as dense massive aggregates, and it contains a certain amount of chromium (Cr) (Fig. 7C). Altered magnetite may also be present as nodular/earthy aggregates (Fig. 7D). Both types of magnetite have relatively high Cl concentrations (Fig. 7C, D), consistent with its interaction with the volatile component of a magmatic system, e.g., during magma cooling and crystallization (Wang et al., 2014). Tourmaline is present as prisms, irregular fragments, and sub-rounded to round grains (e.g., Fig. 7E). The presence of iron and magnesium and the dark color are consistent with Fe, Mg-tourmaline (Henry and Guidotti, 1985). Wolframite, which generally occurs as tabular grains, is a solid solution between the endmembers hübnerite (MnWO4) and ferberite (FeWO4) and shows widely varying chemical compositions. In our samples, Mn ≫ Fe suggests a composition close to the hübnerite endmember (Fig. 7F).

3.5. DTA-TG analysis

The DTA-TG curves for bulk kaolin samples (Fig. 8A) and < 45 μm fractions (Fig. 8B) show similar thermal reactions and are consistent with the results of XRD, SEM, and geochemical analyses. The samples show an endothermal peak at a temperature of ~90–100 °C attributed to the loss of physically adsorbed water in pores, on mineral surfaces (Kakali et al., 2001). Weight loss over the temperature range of 80–350 °C (~0.93% for bulk samples and ~2.07% for the < 45 μm fractions) is associated with a pre-dehydration process, which occurs as a result of reorganization of the octahedral sheet of kaolinite (Cravero et al., 2016). Weight loss over the temperature range of 400–650 °C and an endothermal peak at ~525 °C are evidence of endothermic reactions linked to dehydroxylation of kaolinite and formation of metakaolinite (Cravero et al., 2016). Weight loss over the temperature range of ~600–800 °C may represent complete dehydroxylation of kaolinite and conversion to metakaolinite, or possibly decomposition of alunite. However, SO3 concentrations are low (Table S2) and, assuming that all SO3 is present in alunite, the maximum alunite content would be < 0.1% and, thus, unlikely to be a factor in sample weight loss. An exothermic reaction at ~970–990 °C is due to transformation of metakaolinite to spinel and amorphous silica, and exothermic peaks at 1100–1400 °C are attributed to transformation of metakaolinite to mullite and cristobalite.

4. Discussion

4.1. Supergene kaolinization and associated characteristics of the regolith

None of hypogene indicators (hydrothermal mineral assemblages, shallow igneous activity, mineral zoning, and typical structures such as funnel-shaped, pipelike or elongated zones of kaolinization) are observed in the present study units, and, thus, hypogene kaolinization can be ruled out. Instead, the Chongyi kaolin regolith shows a variety of mineralogic, elemental, and isotopic characteristics typical of surficial weathering, as discussed below.

Kaolinization in the Chongyi regolith is usually associated with minerals produced through low-temperature chemical weathering, e.g., gibbsite, anatase, and iron-oxides. For example, gibbsite, which is typically found in highly weathered soils/sediments, is generated through alteration of aluminosilicate or aluminous minerals under intense weathering conditions (Ramasamy et al., 2014). In addition, tungsten mineralization (here as wolframite) can also be observed. The presence of tourmaline is indicative of high-temperature fractionation within the granite, inconsistent with conditions for kaolinite formation. These minerals can be a weathering residue from a primary high-temperature igneous intrusive body.

SEM observations show that Chongyi kaolinite aggregates are characterized by a variety of morphological features typical of kaolinites produced through supergene weathering processes (Chen et al., 1997; Churchman and Lowe, 2012). Book-like pseudohexagonal kaolinite crystals are commonly due to retention of the original morphology of feldspar crystals (Ekosse, 2001).

Normalized element-distribution patterns do not reveal much about chemical weathering but rather about the parent granite rocks (Fig. 4). However, elemental compositions of the Chongyi kaolin show features typical of surficial weathering. Although Ti and Zr can be released from primary minerals during alteration, they are relatively immobile elements under Earth-surface conditions, and are concentrated more efficiently through chemical weathering (Marfil et al., 2005). In a Zr vs. TiO2 plot, for example, the homogenous kaolin and mottled kaolin samples of the Chongyi deposit fall very close to the supergene field, suggesting a significant surficial weathering contribution (Fig. 9A). Alunite and some aluminum-phosphate-sulfate minerals are common in hypogene deposits, thus these deposits are usually enriched in P and S (Dill et al., 1997). As a result, the rather low P2O5 and SO3 concentrations (Fig. 7C) are consistent with conditions for kaolinite formation. These deposits are usually enriched in P and S (Dill et al., 1997).
concentrations of the Chongyi deposit further demonstrate few influences of hydrothermal alteration (Fig. 9B), consistent with the field observations and XRD analysis. Besides, vertical elemental profiles can also well present supergene chemical characteristics of the Chongyi kaolin regolith (see Section 4.3).

The H and O isotopic compositions of kaolinite provide constraints on the geologic conditions of its formation, assuming no post-depositional alteration has occurred (Savin and Lee, 1988; Gilg et al., 2003; Baioumy, 2013). The oxygen isotopic composition of the kaolin suggests the moderate depth of weathering. In $\delta^{18}$O vs. $\delta^2$H crossplots, the Chongyi samples plot entirely within the supergene field, suggesting significant contribution from chemical weathering (Fig. 5). The global kaolinite weathering line, whose equation is $\delta^2$H = 4.85 × $\delta^{18}$O − 152, represents the isotopic composition of kaolinite in equilibrium with meteoric water at 20 °C (Savin and Epstein, 1970). Most of the Chongyi samples plot very close to the global kaolinite weathering line (Fig. 5), indicating the influence of meteoric waters (Ma et al., 2017). The relationship of $\delta^{18}$O to $\delta^2$H in kaolinites from weathered profiles may permit calculation of a linear equation and isotope fractionation factor (Savin and Lee, 1988; Gilg et al., 2003). The best-fit line for the Chongyi samples is $\delta^2$H = 4.85 × $\delta^{18}$O − 150. Although the $\delta^{18}$O and $\delta^2$H values data of the full sample set are poorly correlated ($r = 0.124$, $n = 9$, $p > 0.1$), the samples with $\delta^2$H $< −60$‰ (which were used to define the best-fit line) exhibit a strong correlation ($r = 0.940$, $n = 5$,

---

**Fig. 6.** SEM images of: (A) poorly crystallized kaolinite (Kaol) with irregular outlines typical of chemical weathering; (B) face-to-face in elongated book-like stacks; (C-E) kaolinite aggregates with vermiform or fan-shaped morphologies; (F) tubular crystals of halloysite (Ha); (G) a sketched diagram shows the progressive transformation of muscovite to kaolinite stacks, involving fan-shaped composite stacks (after Chen et al., 1997). Note that halloysite attached on kaolinite is much less abundant and more sporadic than kaolinite under SEM.
These observations may suggest that minor residual mineral impurities (e.g., quartz and muscovite) with higher $\delta^{2}H$ values (e.g., $>-60$‰) have exerted a measurable influence on the isotopic compositions of some Chongyi samples. Deviations from the global kaolinite weathering line are potentially attributable to post-depositional modifications in weathered profiles (Baioumy, 2013). Such modifications can result from the interactions between earlier-formed kaolinite and downward-percolating meteoric waters (Baioumy, 2013). Another possible cause of deviations is contributions from high-temperature volatiles. Although evidence for such influences is limited in the Chongyi deposit, the presence of Cl-enriched magnetite may be significant in this regard (Fig. 7C, D).

4.2. Kaolin regolith subdivision and mineral weathering

The Chongyi kaolin was developed on a monolithologic and homogeneous protolith (i.e., muscovite granite) without significant sediment inputs. The study area has a tropical monsoonal climate with warm temperatures and high precipitation. Therefore, the Chongyi kaolin deposit can be considered as a "kaolin regolith" (i.e., a residual soil deposit) formed under intense weathering conditions.

Before further discussion of mineral transformations and chemical gradients within the Chongyi regolith, it is necessary to vertically subdivide it and compare its layering with that of typical deeply weathered profiles, as given in Taylor and Eggleton (2001) and Anand and Paine (2002). Regolith consists of a lower saprolith layer and an upper pedolith layer (Fig. 2). The saprolith consists of two layers, saprock below and saprolite above. As suggested by Taylor and Eggleton (2001), the pedolith is more strongly modified through soil-forming processes and is commonly composed (from bottom to top) of a plasmic zone (also referred to as a pallid zone because of its white color), a mottled zone, and a laterite zone (the terms ferruginous duricrust and lateritic residuum may also be used). The pedolith of the...
Chongyi pro file contains a plasmic zone, a mottled zone, and an overlying surface layer (Fig. 2), but the laterite zone that is commonly above the mottled zone is absent. This vertical layering pattern is similar to that of the Yalanbee profile reported by Gilkes et al. (1973). Below this paragraph, we try describing the mottled zone and plasmic zone in the Chongyi regolith in more details with emphasis on some related important mineralogic and geochemical reactions.

The mottled zone, which is found in the middle-upper part of the pedolith (Fig. 2), has cemented segregations of subdominant color different from the surrounding matrix within the Chongyi regolith. The mottles in the Chongyi kaolin have sharp and distinct boundaries, ranging in size from ~5 to ~100 mm. Mottles frequently form due to migration of Fe$^{2+}$ in soil waters and precipitation as Fe$^{3+}$ upon contact with an oxidizing region within the regolith (depending on the depth), which are a common influence on the development of local redox variation within soils and, hence, soil mottling (Taylor and Eggleton, 2001). Based on Taylor and Eggleton (2001), long-term seasonal rise and fall of the groundwater table can lead to reductive mobilization of Fe from the saprolite zone and subsequent precipitation higher in the soil profile upon oxidation at the groundwater table. As a result, the saprolite zone is a major source of Fe for mottle formation.

Below the mottled zone is the homogeneous kaolin zone (Fig. 2), which corresponds to the plasmic zone and is transitional to the underlying saprolite (Gilkes et al., 1973; Anand and Paine, 2002). This zone, which consists mainly of kaolinite, is mesoscopically homogenous owing to destruction of the original sediment fabric (Taylor and Eggleton, 2001). Kaolization of feldspar by chemical weathering is the main source of kaolin (e.g., Gilg et al., 1999; Churchman et al., 2010). Many kaolinite aggregates within regolith (and especially in the plasmic zone) have fan-shaped stacks (Fig. 6C–E), a morphology that is closely associated with transformation of muscovite plates. Feldspar may not directly transform into kaolinite but rather first into muscovite as an intermediate stage under certain geologic conditions (Chen et al., 1997; Lu et al., 2016), which may have been the case for the Chongyi kaolin.

As illustrated in Fig. 6G, the transformation process involves the parallel growth of kaolinite originating from the edges of muscovite grains and subsequent topotactic growth, with the development of fan-shape composite stacks or coalesced stacks. The edges of the kaolinite stacks may split apart into discrete plates (Fig. 6G; Chen et al., 1997). Muscovite of the parent granite can be another important source of kaolinite (Gilkes et al., 1973).

Thermodynamically, the Gibbs free energy of kaolinite formation is slightly lower than that of halloysite formation, so halloysite is less stable than kaolinite (Jeong, 2000; Keeling, 2015). For this reason, if meta-stable halloysite forms, it should do so in advance of formation of the more stable kaolinite phase, due to its lower activation energy of formation (Stumm, 1992). In the Chongyi deposit, however, halloysite is observed to have crystallized after the formation of kaolinite. This apparently contradictory relationship can be ascribed to the presence of weathered mica grains, the surfaces of which provide favorable nucleation sites for kaolinite by significantly reducing its activation energy (Jeong, 2000; Keeling, 2015).

Water-saturated soils in tropical/subtropical climates can lead to abundant halloysite formation (Joussein et al., 2005). Dominance of kaolinite over halloysite in the Chongyi deposit implies a near-surface, freely draining environment (Churchman and Gilkes, 1989; Churchman et al., 2010). However, it is possible that the tubular halloysite crystals

Reference plots of supergene, hypogene, and mixed-type kaolin samples are commonly presence of alunite and some aluminum-phosphate-sulfate minerals in hypogene deposits, they are usually enriched in P and S (Dill et al., 1997). Reference plots of supergene, hypogene, and mixed-type kaolin samples are from Kitagawa and Koster (1991), Dill et al. (1997), and Dill (2015).

within the weathered kaolin directly crystallized from soil waters during periodic waterlogging of microcavities and microfissures, when the activity of aqueous Al and Si did not lead to nucleation of kaolinite on existing mineral surfaces (Chen et al., 1997; Joussein et al., 2005).

4.3. Chemical gradients in the kaolin regolith

The weathering of rock-forming minerals (e.g., feldspar and muscovite) of igneous parent rocks to kaolin is mainly controlled by the chemical composition of the parent rock and the climatic and hydrologic conditions of the supergene environment (Fang et al., 2017). Element mobilization is related to retention and leaching of various elements and to mineral transformations in the principal regolith layers (Tardy et al., 1973; Anand and Paine, 2002; Scott and Pain, 2008). Here, we examine chemical gradients in the Chongyi regolith to investigate how supergene processes influenced and transformed the original kaolin deposit, and to compare them to typical regolith models.

Elemental concentrations in weathered profiles are typically normalized to the concentration of an immobile element such as Ti, Nb, or Zr (White, 1995). In the present case, Ti and Nb are present in rutile and/or anatase, so their concentrations may be influenced by variations in the relative content of these minerals in the host rock. Zr is present almost exclusively in zircons, making it the most suitable element for normalization. The relative gains and losses of elements were calculated based on the assumption of immobility of Zr.

The mass transfer coefficient \( \tau_{i,j} \) quantifies elemental changes in regolith profiles, accounting for both volume changes and relative gains or losses of elements (Anderson et al., 2002):

\[
\tau_{i,j} = \frac{C_{i,w}}{C_{i,p} - C_{i,w}} - 1
\]

where \( C \) represents concentration of mobile (i) or immobile (j) elements in parent (p) or weathered (w) material. Negative \( \tau_{i,j} \) values suggest depletion of element \( j \), positive values mean enrichment, and when \( \tau_{i,j} = 0 \), the concentration of an element is identical to that of the parent material. We used the underlying weakly altered granite (saprolith; Anand and Paine, 2002) as the parent material in calculating the elemental profiles of Fig. 10.

Elemental profiles are one of the most important lines of evidence for assessing pedogenic processes in regoliths. The patterns of elemental changes with depth can be assigned to specific endmember types (Brantley et al., 2008; Brantley and White, 2009), of which four are recognized: (1) Depletion profiles develop for elements that are strongly depleted in the pedolith (mostly in the upper levels of the regolith), usually due to mineral dissolution, and without reprecipitation at depth (Fig. 10A). For example, Na commonly exhibits a depletion profile owing to weathering of plagioclase feldspar (White, 1995) and a lack of reprecipitation in illuviated oxides or clay minerals. (2) Depletion-enrichment profiles develop for elements that are leached in an upper regolith layer but reprecipitated at depth (Fig. 10B). For example, Al is commonly mobilized as colloids and organic complexes in the surface layer and then redeposited deeper in a regolith profile (e.g., mottled kaolin zone), where concentrations of organic ligands are lower (Brantley and White, 2009). (3) Addition profiles develop for elements that are added to the regolith surface layer through atmospheric deposition, and which are redistributed downward through leaching or mixing processes (Fig. 10C). Addition profiles are characterized by peak concentrations at the top of the regolith profile and declining concentrations at depth. For example, Mn profiles can be dominated by wet or dry deposition from the atmosphere (Herndon et al., 2011). (4) Biogenic profiles exhibit trends that are opposite to depletion-enrichment profiles (Fig. 10D). They show peak enrichments at or close to the top of the regolith profile owing to the effects of organic acid secretion by plants or fungi and the consequent dissolution and uptake of nutrient elements (Brantley and White, 2009). If the released nutrients (e.g., Ca) are taken up by roots, or recycled in the upper layer of soil, a biogenic profile develops (Jobbagy and Jackson, 2001).

These four types of elemental profiles tend to be distinctly developed in thin in situ regoliths, whereas deeply weathered (thick) regoliths formed on granite host rocks may show different chemical profiles (e.g., Gilkes et al., 1973; Davy and El-Ansary, 1986; Anand and Paine, 2002; Scott and Pain, 2008). The weathering behavior of elements in thick granite-derived regoliths has been summarized by Davy and El-Ansary (1986) and Anand and Paine (2002). Here, we compare four elements (i.e., Na, Al, Mn, and Ca) representing different types of elemental profiles in the Chongyi regolith with those from published sources (Fig. 10).

Elemental profiles of mobile elements such as Na exhibit similar patterns in both the Chongyi kaolin and deeply weathered profiles (reference profiles; Fig. 10A). These elements are characterized by leaching and depletion throughout the regolith, without reprecipitation at depth. Elemental profiles of elements like Al show different patterns in the two types of regolith: they are leached from upper levels (e.g., mottled kaolin zone) and reprecipitated at depth in the Chongyi kaolin, whereas they are generally residually enriched towards the surface layer in the reference profiles (Fig. 10B). Elements such as Mn are leached and depleted at deeper levels (e.g., in the saprolith) in both types of regolith, and they are enriched in the upper part of the Chongyi regolith (e.g., mottled kaolin zone); but they are residually enriched throughout the reference profiles (Fig. 10C). Elemental profiles of elements like Ca exhibit similar patterns in both types of regolith, and these elements are reprecipitated/enriched at or close to the top of the profile (Fig. 10D).
4.4. Implications for formation of kaolin regolith and supergene pedogenesis

Previous studies on various argillization, in particular kaolin, focus more commonly on its economic value, compared to systematic studies regarding pedological, mineralogic, and geochemical processes taking place in kaolin regoliths (Ekosse, 2001; Anand and Paine, 2002; Scott and Pain, 2008). This would limit our understanding of kaolin argillation linked to supergene processes in the Earth’s surface environments. In this study, we demonstrated that the kaolin regolith from subtropical China was derived from supergene weathering processes using integrated mineralogic and geochemical analyses.

While the kaolin regolith can be subdivided into several layers with reference to typical subdivision of the deeply weathered profile, their elemental profiles are not necessarily uniform with those of typical deep granite weathering profiles. Instead, they are generally consistent with those of relative thin in situ soil systems as widely reported previously. The four types of elemental profiles reflect chemical gradients in the kaolin regolith as well as some biological effects (depending on the depth). These elemental patterns are affected by a combination of chemical, geologic, and biologic processes that control soil formation and evolution (Brantley and White, 2009). That is to say, the supergene kaolin regolith is intrinsically more similar to shallow, biologically active residual soil deposits, rather than the deep granite weathering profiles.

Based on the discussion above, we propose a model to illustrate geological evolution, mineralogic transformation, and elemental migration within the kaolin regolith in particular linked to supergene processes (Fig. 11). Kaolin may form in semi-humid to humid mid-latitude climate zones with moderate to intense weathering intensity, but chemical weathering alone in such settings are usually unable to initiate supergene kaolinization. The initial processes of weathering could be physical, for example, the development of physical openings along joints, which may produce small fragments moving locally (Fig. 11; Taylor and Eggleton, 2001). Strong weathering conditions typical of humid subtropical/tropical climate zone with high MAT and MAP (e.g., the Chongyi region) favor supergene argillization. As chemical weathering occurs, solutes are moved by solutions passing through the granite. The exposed kaolin experienced enhanced weathering under such climatic conditions, resulting in new regolith formation (Fig. 11).

5. Conclusions

Three kaolin-regolith drillholes from a subtropical climate zone in southern China were investigated using an integrated mineralogic, elemental, and isotopic geochemical approach. Neither shallow level of granite emplacement, representative structural controls on kaolinization, mineral zoning, nor hypothermal minerals can be observed. The mineral assemblages display typical supergene characteristics, and kaolinite mineral aggregates are characterized by a variety of morphological features suggestive of supergene weathering. Geochemical binary plots (e.g., Zr vs. TiO₂, P₂O₅ vs. SO₃, and δ¹⁸O vs. δ²H) also point to a supergene origin for the kaolin regolith. Numerous kaolinite aggregates within regolith have fan-shaped stacks, a morphology that is tightly associated with transformation of muscovite plates. Dominance of kaolinite over halloysite implies a near-surface, freely draining environment.

Four types of regolith elemental profiles can be identified in the kaolin regolith: depletion (e.g., Na), depletion-enrichment (e.g., Al),
addition (e.g., Mn), and biogenic (e.g., Ca) profiles. These profiles reflect chemical gradients in the kaolin regolith as well as some biological effects that are typical of relative thin in situ soil systems. However, the elemental profiles are not necessarily consistent those of typical deep (thick) granite weathering profiles. Strong weathering conditions, typical of humid subtropical/tropical climate zone with high MAT and MAP favor supergene argillization, resulting in new kaolin regolith formation.

Acknowledgments


Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geoderma.2018.09.020.