

A NEW LOOK AT THE OCCURRENCES OF THE RARE-EARTH ELEMENTS IN THE GEORGIA KAOLINS

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Abstract—The high-density siliciclastic minerals (*e.g.* zircon) in the coarse fractions (>44 μm , informally known as grit) of the mined Georgia kaolins are potential and significant sources of the rare-earth elements (*REE*). The abundances and provenance of the *REE* signature have not been studied extensively for the Georgia kaolins. The objective of the present study was, therefore, to define the contribution of these heavy minerals (*e.g.* zircon) to the *REE* inventory of the coarse fractions of Georgia kaolins. Heavy-mineral subfractions separated from the coarse fractions contained 1647 mg/kg *REE* from the Jeffersonville Member of the Lower Tertiary Huber Formation and 5012 mg/kg *REE* from the Buffalo Creek Kaolin Member of the Upper Cretaceous Galliard Formation, respectively. These heavy-mineral subfractions were enriched 10–100 times in the heavy rare-earth elements (*HREE*, Gd–Lu), Hf, and Zr relative to the concentrations of these elements in Upper Continental Crust. The heavy-mineral subfractions comprised 5% of the coarse fractions (grit) of these two kaolin-producing formations. The heavy-mineral subfractions consisted of zircon, anatase, rutile, kaolinite, and minor amounts of muscovite, trace ilmenite, and staurolite. The large concentrations of *REE* were obtained by separating the dense heavy minerals from the coarse fraction (grit) obtained during the typical production of kaolin-group minerals (kaolinite) from kaolin ore. The amount of zircon (estimated from the 6–11 wt.% Zr) and the absence of monazite did not explain the high concentrations of *REE* in the heavy-mineral subfractions. The large amounts of *REE* could have resulted from the sorption of *REE* released during weathering reactions, or from the presence of small amounts (0.025 wt.%) each of monazite and xenotime in addition to the presence of zircon. This heavy-mineral subfraction represented a novel domestic resource of extractable *REE*, especially the *HREE*, of a grade as high as 0.50 wt.% total *REE*.

Key Words—Georgia, Heavy Mineral Separation, Kaolin, Rare-Earth Elements.

INTRODUCTION

Investigations of the presence of *REE* in the Georgia kaolin deposits are needed, given cessation of domestic *REE* mining in 2016 (Gambogi, 2017), the increased demand for *REE* for the development of many advanced technologies and materials, and the large percentage (90%) of *REE*, especially *HREE*, imported to the United States from mining both hard-rock and *HREE*-rich laterite deposits in China (Kynicky *et al.*, 2012; Weng *et al.*, 2015). As a result, non-conventional sources have been explored to secure reliable domestic sources of *REE*. Examples of non-conventional sources of *REE* include residues from coal combustion, ocean water, and regoliths (Foley and Ayuso, 2015; Drost and Wang, 2016; Rozelle *et al.*, 2016; Bern *et al.*, 2017). Georgia kaolin deposits have represented known and significant sources of the *REE*, especially of the light rare-earth elements (*LREE*, La–Nd; Dombrowski, 1992; Cheshire, 2011). Results presented here show the enrichments in the *HREE* (Gd–Lu) in the heavy-mineral subfractions of the coarse fractions, informally known as grit, of the Georgia kaolins.

The observed assemblages of the *REE* in argillaceous rocks, soils, and sediments are known to be a function mostly of inheritance from parent rocks or detrital minerals given their insolubility and the insolubility of the minerals containing *REE* (*e.g.* Gromet *et al.*, 1984). The observed *REE* contents in argillaceous rocks and soils resulted also from fractionation per density or size fraction during transport and deposition (Cullers *et al.*, 1979; McLennan, 1989). Chemical weathering processes led to loss, redistribution, or fractionation of the *REE* (Burkov and Podporina, 1967; Banfield and Eggleton, 1998; Aubert *et al.*, 2001; Papoulis *et al.*, 2004; Sousa *et al.*, 2006; Ma *et al.*, 2011; Cheshire, 2011; Bern *et al.*, 2017), *e.g.* the accumulation of *HREE* and a concomitant loss of the *LREE* arising from the continued alteration of a granitic residuum to kaolin-rich clay was noted by Burkov and Podporina (1967). The accumulations of *REE* in weathered rocks were enriched in the *LREE* or in the *HREE* depending on the *REE* composition and solubility of primary minerals being weathered (Bao and Zhao, 2008, and references therein). The *REE* in laterites from eastern and southeastern China (Jiangxi Province) comprise ~80% of the present known reserves of *HREE* (Kynicky *et al.*, 2012; Li and Yang, 2016). These laterites contained 0.05–0.5 wt.% total *REE* and are enriched in *HREE* (Li and Yang, 2016). The *REE* sorbed on pedogenic mineral surfaces were desorbed easily

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(Moldovenau and Papangelakis, 2012). Lastly, subsequent diagenetic processes also impacted the distribution of *REE* in argillaceous rocks (e.g. Awwiller and Mack, 1991; Elliott, 1993; Ohr *et al.*, 1994; Lev *et al.*, 1999; Bechtel *et al.*, 2001; Oszczepalski *et al.*, 2016).

In the southeast United States, the *REE*-bearing minerals (e.g. xenotime, monazite) were found associated with mature minerals in alluvial sediments and beach sands (Bern *et al.*, 2016). In addition to these placer deposits, the Georgia kaolin deposits represented a possible exploration target for *REE* given their highly weathered character and the presence of mineralogically mature and heavy minerals such as tourmaline, magnetite, monazite, leucoxene, zircon, and rutile (Murray, 1976). The Cretaceous Buffalo Creek Kaolin Member of the Galliard Formation (hereinafter Buffalo Creek Kaolin Member) and the Tertiary Marion Member of the Huber Formation have been found to contain enrichments in the *LREE* relative to both the North American Shale Composite (NASC) and to the Georgia Saprolite Composite (GASC; Cheshire, 2011). Saprolite materials have been suggested as a possible source material for the Georgia kaolins (Cheshire, 2011). High concentrations of La (81–463 mg/kg), Sc, Co, and Th in both the Cretaceous and Tertiary kaolin members were found by Dombrowski (1992). Secondary phosphate minerals containing rare-earth elements (crandallite and florencite, gorceixite, xenotime) have been observed in fine-silt fractions of the Georgia kaolins (Cheshire, 2011).

The provenance of *REE*-containing minerals within the Georgia kaolins was difficult to determine due to the uncertainties of the effects of remobilization of *REE* and other trace constituents in fine fractions of kaolins (e.g. Dombrowski, 1992; Cheshire, 2011). The present study

examined the contribution of *REE* from the coarse (>44 μm) discarded gangue materials, informally referred to as “grit” (Murray, 2007), from representative samples collected from the Cretaceous Buffalo Creek Kaolin Member and from the Jeffersonville Member. These two formations were mined actively for kaolin in Georgia (Elzea-Kogel *et al.*, 2000). This geochemical and mineralogical study showed enrichments of the *REE* relative to Upper Continental Crust (UCC) in the heavy-mineral subfraction separated from the coarse fractions (>44 μm). The use of a heavy liquid (lithium metatungstate, LMT) resulted in the separation of potentially mineable concentrations of the *REE* (1600–5000 mg/kg total *REE*), especially the *HREE*. Given that this coarse fraction (*i.e.* ‘grit’) had already been separated during the processing of kaolin ore to a kaolinite product (Murray, 2007), the *REE* and *HREE* could, conceivably, be co-produced during the normal processing of kaolin ore. The objective of the present study was to define the contribution of these heavy minerals (e.g. zircon) to the *REE* inventory of the Georgia kaolins. The results obtained permitted the derivation of two hypotheses to explain the presence of *REE* in these coarse (grit) fractions of the Georgia kaolins: (1) inheritance in clastic minerals (e.g. zircon, monazite, xenotime); and (2) sorption of *REE* onto mineral surfaces.

Pertinent general geology of the Georgia kaolins

The Georgia kaolin deposits are located in a geographic area 40 km wide and 240 km long extending from Anderson, Georgia, to Aiken, South Carolina, in the Atlantic Coastal Plain, 32–64 km south of the Fall Line contact between the Coastal Plain and the Piedmont Province (Prasad *et al.*, 1991; Figure 1). The kaolin was mined from lenses of kaolin-rich clay found within

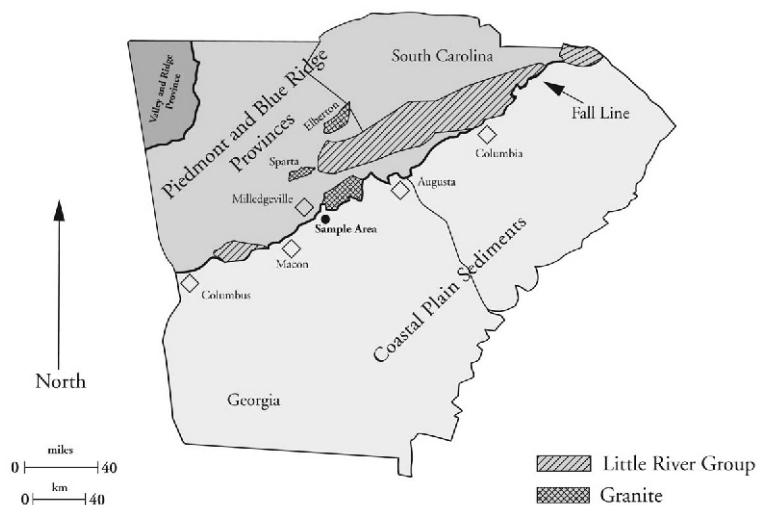


Figure 1. Map of the geologic provinces in Georgia showing Valley and Ridge, Blue Ridge-Piedmont, Fall Line, and Coastal Plain. The positions of the Sparta Granite and other granite bodies, and the Little River Group are noted relative to the position of the Avant Mine and Sara Dukes Mine (sample area). Map modified from Dombrowski (1992).

deltaic sands of the Upper Cretaceous and the Paleogene (Paleocene and Eocene) Oconee Group. The thickness of the Oconee Group increased from <1 m at the Fall Line to as much as 800 m in a down-dip direction from the Fall Line where they interfinger with marine and offshore sediments (Elzea-Kogel *et al.*, 2000). The kaolin lenses were 1–30 m thick by hundreds of thousands of square meters in areal extent (Elzea-Kogel *et al.*, 2000). The kaolin ore within the Oconee Group was mined mostly (70%) from the Upper Cretaceous (Campanian) Buffalo Creek Kaolin Member while the remainder (30%) was mined from the Jeffersonville Member of the Paleocene–Eocene Huber Formation (Huddleston and Hetrick, 1991; Elzea-Kogel *et al.*, 2000). A soft, coarser-grained kaolin with conchoidal fracture was mined from the Upper Cretaceous Buffalo Creek Kaolin Member. A hard, finer-grained kaolin was mined from the Jeffersonville Member (Middle Eocene) of the Paleogene Huber Formation. The Cretaceous Buffalo Creek Kaolin Member was underlain unconformably by arkose sand and gravel belonging to the Cretaceous Pio Nono Formation. The Pio Nono, in turn, was underlain by Piedmont crystalline rocks (Elzea-Kogel *et al.*, 2000). The Jeffersonville Member of the Huber Formation, the top of the Oconee Group, was overlain by the Clinchfield Sand (Carver, 1966) and by marine sediments of the Twiggs Clay Member of the Dry Branch Formation (Shearer, 1917; Huddleston and Hetrick, 1979). The Buffalo Creek Kaolin Member consists of cross-bedded, fining-upward, channel fill of gravel, sand, silt, and kaolin clay lenses. Discontinuous lenses of kaolin clay <1 km long were found in the uppermost part of the Buffalo Creek (Huddleston and Hetrick, 1991). The Buffalo Creek was overlain unconformably by the Marion Member of the Huber Formation. The Marion Member of the Huber Formation contained a basal conglomerate of pebbles and kaolin clasts at the base. The sandy base graded to a clay-rich zone with lignite seams. The Marion Member has not been mined extensively for kaolin. Hard, fine-grained kaolin lenses enclosed by brackish, intertidal sands were found near the top of the Jeffersonville Member. These hard kaolins show extensive amounts of trace fossils (shrimp) and bioturbation features (Schroder, 1982; Elzea-Kogel *et al.*, 2000).

The origin of the Georgia kaolin deposits is controversial. The Coastal Plain sediments hosting these kaolin deposits adjacent to the Fall Line are projected to be located close to or within a hydrologic recharge zone for Coastal Plain sedimentary rocks (Hurst and Pickering, 1997). The presence of this hydrologic recharge zone supported the formation of these kaolins by a pervasive *in situ* chemical weathering of Coastal Plain sediments resulting in residual kaolin. Relict features of bedding, cross-bedding, and even upward-fining cycles were seen in exposures of the mined

kaolins. These relict sedimentological features provided a framework for a depositional origin of clastic grains of kaolinite and the presence of thick clay lenses within these deltaic sand deposits (Dombrowski, 1993; Elzea-Kogel *et al.*, 2000). Such clastic kaolinite could have been produced originally as residual grains formed by chemical weathering within the Piedmont Province. These kaolinite grains and other siliciclastic minerals were then transported from the Piedmont Province by fluvial processes and deposited in the Coastal Plain. Trace-element studies have pointed to possible sources of the kaolin in the kaolin lenses. Based on a comparison of trace-element chemistry (Th, in particular; Dombrowski, 1992), the trace-element composition of the soft kaolins was similar to that of the local Piedmont granite and gneiss (*e.g.* Sparta Granite and its kaolinite-rich saprolite, Figure 1). The trace-element composition of the hard kaolins in eastern Georgia and South Carolina were similar to the trace element compositions of both gneiss and phyllite (Figure 1; Dombrowski, 1992, 1993; Elzea-Kogel *et al.*, 2000).

Georgia is a leading domestic producer of kaolinite (*e.g.* 5450 thousand metric tons in 2016; Virta, 2015; US Geological Survey, 2016). A large fraction of the kaolin mined from this region is used for paper coating and paper products. Smaller proportions of the mined kaolins are used in the base material for fiberglass and ceramics (Elzea-Kogel *et al.*, 2000; Virta, 2015). Proppants, composed of fired kaolin clay, are new products developed for the hydrofracturing of black shales (Virta, 2015). Kaolin reserves are typically held as proprietary information by the producers (D. Flanagan, USGS, pers. comm., 2017). A reserve of 60–75 million tons of kaolin clays was determined for the Irwinton District of Georgia (Lang *et al.*, 1965).

METHODS

A representative sample of the Cretaceous Buffalo Creek Kaolin Member of the Galliard Formation was collected from the Avant Mine located at ~32°58'N83°03'W. A representative sample of the Eocene Jeffersonville Member of the Huber Formation was collected from the Sara Dukes Mine located at ~32°56'N 82°56'W. The locations of these mines are shown as one sample location (Figure 1). These samples were processed to separate the coarse (>44 μm) gangue minerals from the mined kaolin (Gardner, 2016). Crushed raw kaolin ore was blunged (dispersed) at 35% solids in deionized water containing 0.25 wt.% Na-hexametaphosphate dry/dry clay weight basis and 0.05 wt.% sodium carbonate dry/dry clay basis (Fisher Scientific, Pittsburgh, Pennsylvania, USA) in a Morehouse Cowles Dissolver (Morehouse Cowles, Chino, California, USA). This blunged slurry was allowed to settle for 2.5 min/cm suspension to concentrate the coarse fraction. The top fine fraction

(supernatant) was siphoned off and discarded. The remaining sand-silt fraction was screened through a 325 mesh sieve ($>44\ \mu\text{m}$). The $>44\ \mu\text{m}$ fraction of the Buffalo Creek Member was washed in water and dried at 50°C . The Jeffersonville Member coarse fraction contained a significant amount of unblunged clay ('pin heads'). This fraction was re-suspended in a Waring blender at 10% solids. A small amount of Na-hexametaphosphate and sodium carbonate was added and mixed for 3 min. This suspension was screened through 325 mesh and washed again. The coarse fraction ($>44\ \mu\text{m}$) was dried at 50°C as was the Buffalo Creek sample. The two coarse ($>44\ \mu\text{m}$) fractions obtained from this process are referred to here as "BC CF" and "JV CF" representing Buffalo Creek Kaolin Member (BC CF) and the Jeffersonville Member (JV CF), respectively. Further details of these separations were described by Gardner (2016).

The two coarse fractions (BC CF and JV CF) were then separated further into the light ($<2.95\ \text{kg/L}$) mineral and the heavy ($>2.95\ \text{kg/L}$) mineral subfractions *via* heavy-liquid separation using lithium metatungstate (LMT, $\rho = 2.95\ \text{kg/L}$, LMT Liquid, LLC, Idaho Falls, Idaho, USA). This liquid was chosen due to its low price and low volatility relative to other separatory fluids (Totten *et al.*, 2002). The density separation was accomplished by mixing 20–30 g of the coarse fraction with LMT in a KIMAX[®]-liter separatory funnel (Fisher Scientific, Pittsburgh, Pennsylvania, USA). This mixture was covered with plastic wrap and left overnight to allow mineral grains with densities of $>2.95\ \text{kg/L}$ to settle to the bottom of the funnel while mineral grains with densities $<2.95\ \text{kg/L}$ floated to the top of the LMT liquid in the separatory funnel. After settling overnight, the heavy grains which settled at the bottom of the separatory funnel were drained carefully into a funnel lined with Number 2 filter paper (Fisher Scientific, Pittsburgh, Pennsylvania, USA). Number 2 filter paper was used to ensure the retention of sand-sized grains and any coarse silt material in the heavy-mineral fraction which was rinsed three times using deionized water. The rinsed filters were then placed in an oven at 50°C for ~2 h or until dry. The light grains, which remained within the separatory funnel, were then drained, rinsed, and dried using the same procedure. These separations yielded four subfractions referred to throughout as: the Buffalo Creek light mineral subfraction (BC LF), the Buffalo Creek heavy mineral subfraction (BC HF), the Jeffersonville heavy mineral subfraction (JV HF), and the Jeffersonville light mineral subfraction (JV LF). The mineralogical compositions of the heavy and light mineral subfractions were determined using X-ray diffractometry. A Panalytical X'pert Pro X-ray diffractometer, equipped with the X'pert HighScore[®] software (Malvern Panalytical B.V., Almelo, The Netherlands), housed in the Geosciences Department of Georgia State University (GSU), was used in this present study.

Randomly oriented mounts of the heavy-mineral and light-mineral subfractions ($<0.25\ \text{g}$) were deposited onto petrographic slides using a 4 mL disposable plastic pipette with deionized water and dried at 50°C (Moore and Reynolds, 1997). These mounts were scanned from $5\text{--}60^\circ 2\theta$ at $1^\circ 2\theta\ \text{min}^{-1}$ using Ni-filtered Cu radiation. The X'pert HighScore[®] software was used to assist in mineral identification and to permit semi-quantification of the minerals. Phase identification data, noted in several prominent texts, were consulted to identify the mineral phases (Brown and Brindley, 1980; Jackson, 1985; Moore and Reynolds, 1997). Semi-quantitative data did not match well the major-element data. The amounts of the minerals present were estimated using the MINSQ spreadsheet program (Herrmann and Berry, 2002). This spreadsheet employed a least-squares fit algorithm. An acceptable determination of mineral proportions in these subfractions had a Sum of Squares Residual value of 0.0–0.1. The amount of zircon was estimated through conversion of the measured Zr content with the appropriate gravimetric factor to convert Zr to ZrSiO_4 . No other phases containing significant amounts of Zr were present in these samples. The contributions of REE and HREE from zircon were estimated from the product of the estimated zircon content and the maximum total REE (2500 mg/kg) present in zircon (Hoskin and Schaltegger, 2003). The weighted sum of REE from a mixture of zircon (99.5 wt.%), xenotime (0.25 wt.%), and monazite (0.25 wt.%) was calculated using values of REE in zircon, monazite, and xenotime (Bea, 1996; Epperson and Elliott, 2018). The weighted sums of REE normalized to UCC were compared to the REE normalized to UCC of the Buffalo Creek heavy subfraction.

The heavy-mineral and light-mineral subfractions of both grit samples were examined by scanning electron microscopy (SEM) using a LEO 1450v Scanning Electron Microscope with a Rontec (SD type) detector (Carl Zeiss Microscopy, Oberkochen, Germany) along with Energy Dispersive Spectrometer software (EDS) from IXRF Systems (Austin, Texas, USA). The microscope is housed in the Imaging Core Facility, Biology Department, Georgia State University and was used for element identification. The samples of the light mineral fractions were coated in carbon. Samples of the heavy-mineral separates were coated with gold (15 nm thick). An acceleration voltage of 15 kV was used in the analysis of the light-mineral fraction while a voltage of 30 kV was utilized in the analysis of the heavy-mineral subfraction.

Samples of the coarse fraction, the heavy-mineral subfraction, and the light-mineral subfractions for both the Buffalo Creek and Jeffersonville Member kaolins were analyzed for major, trace, and rare-earth elements by Activation Laboratories (Ancaster, Ontario, Canada) using inductively coupled plasma-mass spectrometry (ICP-MS)-based methods. Numerous certified standards

were analyzed by Activation Laboratories in conjunction with the analyses for this present study, including DNC-1 (Flanagan, 1984), W-2a (Flanagan and Gottfried, 1980), SY-4 (Bowman, 1995), and BIR-1a (Flanagan and Gottfried, 1980) for the major element analyses; W-2a (Flanagan and Gottfried, 1980) and JR-1 for trace elements (Imai *et al.*, 1995); and NCS DC86312, NCSDC86318 (China National Analysis Center for Iron and Steel, 2008), OREAS100 (Ore Research and Exploration Pty Ltd., 2008a), and OREAS101 (Ore Research and Exploration Pty Ltd., 2008b) for the lanthanide rare earth metals. The REE analyses for the North American Standard Shale Composite (NASC, Gromet *et al.*, 1984), Upper Continental Crust (UCC, Rudnick and Gao, 2003), Georgia Saprolite Composite (GASC, Cheshire, 2011), and C1 Chondrite (Anders and Grevesse, 1989) were given with the measured results. The results were normalized primarily with respect to UCC given the larger abundances of REE and many lithophile trace elements in continental crust compared to C1 chondrite. The REE concentrations in UCC are similar to the REE concentrations for the NASC (*e.g.* Piper and Bau, 2013). The REE include the lanthanide series (La–Lu), Y, and Sc as per the International Union of Pure and Applied Chemistry (IUPAC).

An estimate of REE resources from the Georgia kaolins was calculated knowing the amount discarded (grit) during mining and processing of kaolin ore, the fraction of the coarse fraction in the Buffalo Creek and in the Jeffersonville Member (0.10 g/g kaolin), the fraction of heavy-mineral subfraction (0.05 g heavy mineral fraction/g coarse fraction; Gardner, 2016), and the total REE in the heavy-mineral subfractions. The amount of material discarded from kaolin mining is

typically 30% of that mined (pers. comm., E. Riley, 2017). The amount of kaolin produced (*i.e.* 5450 thousand metric ton/y, or 5450×10^{12} g/y; Virta, 2015) represents 70% of the amount mined. The amount mined was calculated at 7.7×10^{12} g/y. The amount discarded, therefore, was estimated as 2.3×10^{12} g/y corresponding to 30% of the amount mined.

RESULTS

Mineralogy

The sand and silt minerals in the heavy and light mineral subfractions were clear and without any coatings of clay (Figure 2a–c). Some light minerals were found in the heavy-mineral subfractions. No heavy minerals were found in the light-mineral subfractions, based on XRD analyses (Figure 3a–3d). The Buffalo Creek Kaolin Member heavy-mineral fraction contained zircon, rutile, anatase, quartz, staurolite, ilmenite, and apatite, based on SEM and XRD analyses (Figures 2a–b, 3a, Table 1). The light-mineral subfraction of the Buffalo Creek Kaolin Member consists of kaolinite, muscovite, and quartz (Table 1, Figure 3b). The mineral proportions, as per *MINSQ* (wt.%), for the Buffalo Creek Kaolin Member heavy subfraction were: 52.9% rutile plus anatase, 10.3% ilmenite, 6.8% staurolite, 4.5% quartz, 1.2% zircon, and 3.4% other phases in small/trace amounts (xenotime, monazite, and apatite, Table 1). The mineral proportions for the light-mineral subfraction of the Buffalo Creek Kaolin Member were: 83.2% kaolinite, 6.0% staurolite, 3.3% quartz, 2.2% muscovite, and 0.8% rutile (Table 1).

According to XRD, the Jeffersonville Member heavy-mineral subfraction contained quartz, muscovite, kaolinite, rutile, anatase, zircon, and apatite (Figure 3c). The

Table 1. Summary of phase identification and mineral-proportion determinations.

		Minerals present (XRD)								
		Mineral-proportion analyses (<i>MINSQ</i>)								
		Qtz	Rutile	Zircon	Staurolite	Ilmenite	Muscovite	Kaol.	Other	SSQ
BC HF	Anatase, apatite, kaolinite, ilmenite, rutile, staurolite, zircon									
BC LF	Kaolinite, muscovite, quartz									
JV HF	Anatase, apatite, muscovite, quartz, rutile, zircon									
JV LF	Quartz, muscovite									
BC HF		4.5	52.9	1.2	6.8	10.3	0.3	0	3.4 ¹	0.0
BC LF		3.3	0.8	–	6.0	–	2.2	83.2	–	0.1
JF HF		26	13.2	0.7	26.6	11.0	4.1	–	9.1 ²	0.1
JF LF		92.3	–	–	0.5	1.3	2.3	3.0	1.3 ³	0.1

Notes. BC– Buffalo Creek Kaolin Member, JV – Jeffersonville Member, HF – heavy mineral subfraction, LF – light mineral subfraction, Qtz – quartz, Kaol. – kaolinite. SSQ – sum of squared residuals (Herrmann and Berry, 2002).

¹ – xenotime, monazite, and apatite; ² – monazite and hornblende; ³ – albite.

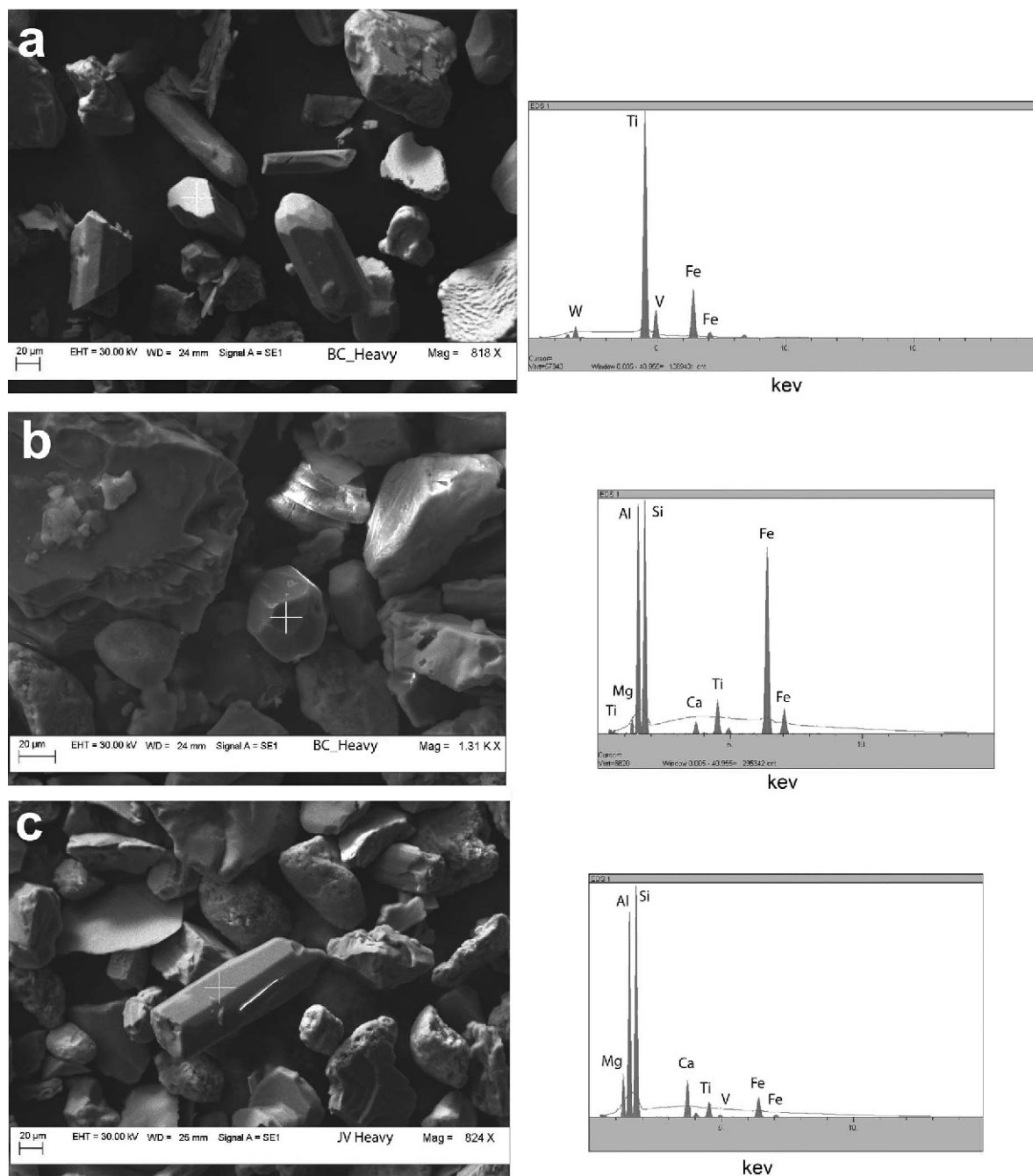


Figure 2. SEM images and EDS spectra: (a) ilmenite in Buffalo Creek Kaolin Member heavy subfraction; (b) a fragment of a phase containing Si, Fe, Ti, Ca, Al, and Mg identified tentatively as a fragment of staurolite in the Buffalo Creek Kaolin Member; (c) fragment of hornblende in the heavy fraction of the Jeffersonville Member. The grains are highly weathered and rounded in the Jeffersonville Member.

proportions of these minerals as per *MINSQ* calculations were: 26.6% staurolite, 26% quartz, 13.2% rutile, 11% ilmenite, 4.1% quartz, and 9.1% other phases (Table 1). The other phases included in the calculated mineral proportions are monazite and hornblende (Figure 2c, Table 1). The Jeffersonville Member light subfraction

contained quartz, muscovite, and kaolinite (Figure 3d). According to *MINSQ* calculations, quartz was the most abundant phase in this light subfraction (92.3%, Table 1). This quartz showed more rounded and smaller grain sizes than the grains in the Buffalo Creek Kaolin Member. Smaller amounts of muscovite (2.2%), kaolin-

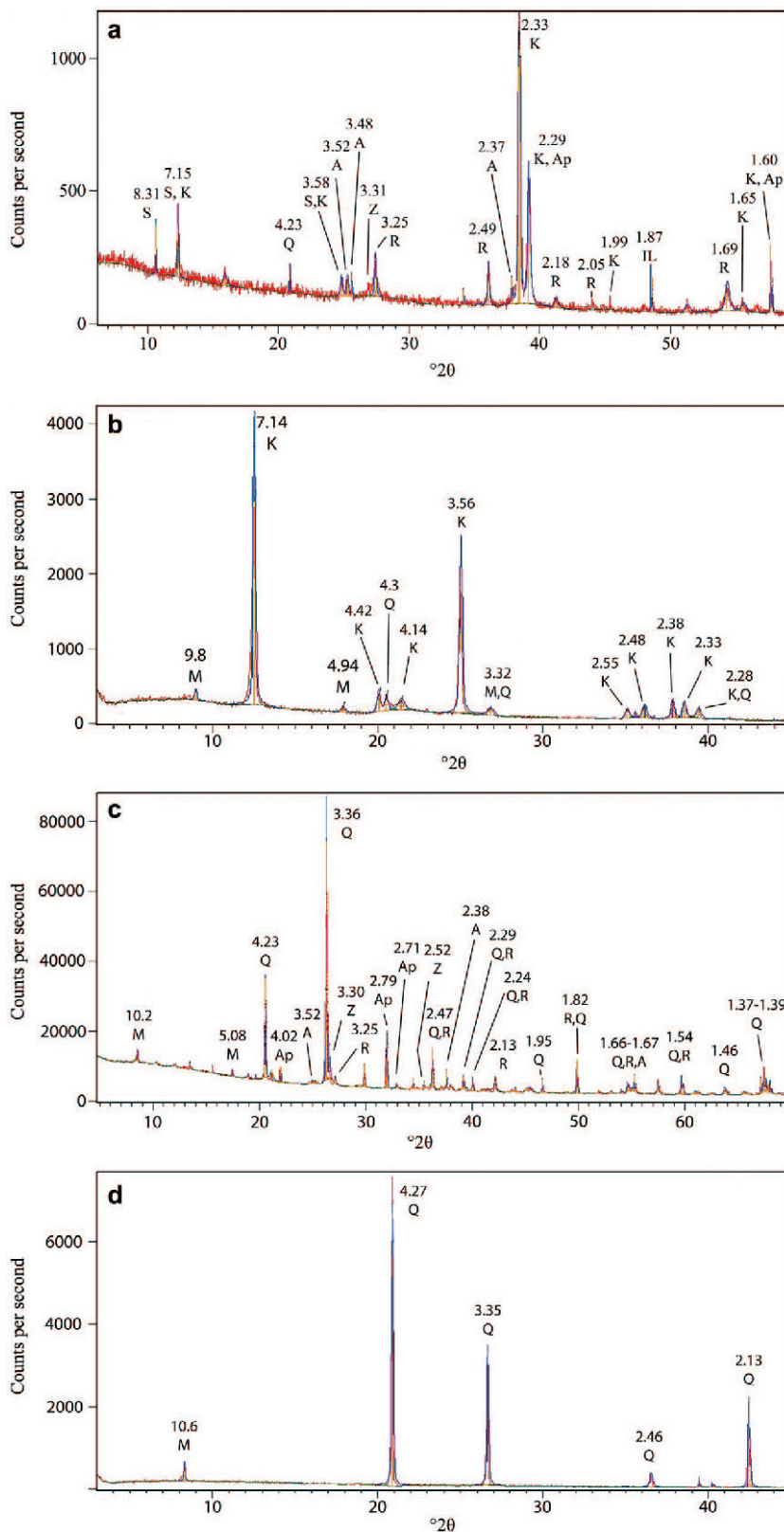


Figure 3. XRD traces for: (a) the heavy-mineral fraction of the Buffalo Creek Kaolin Member; (b) the light-mineral subfraction of Buffalo Creek Kaolin Member; (c) the heavy-mineral subfraction of the Jeffersonville Member; and (d) the light-mineral subfraction of the Jeffersonville Member.

ite (3.0%), and trace amounts of ilmenite (1.3%), staurolite (0.5%), and albite (1.3%) were present per *MINSQ* (Table 1).

Elemental analyses

Major element, trace element, and *REE* analyses are summarized in Tables 2–4 for the heavy-mineral subfractions, light-mineral subfractions, and coarse fractions for the Buffalo Creek Kaolin Member and Jeffersonville Member samples. The major- and trace-element compositions of the Buffalo Creek Kaolin Member heavy-mineral subfraction contained large amounts of TiO_2 (58 wt.%) and Zr (56,430 mg/kg, 8.24 wt.% ZrO_2 or 11 wt.% zircon assuming no other Zr-bearing phases were present). These major-element analyses were consistent with the amounts of rutile and anatase (53%) calculated. The percentages of zircon derived from the major element analyses were greater than the calculated amount of zircon (1.2%, Table 1).

The major-element composition of the Jeffersonville Member heavy-mineral subfraction contained sizable amounts of TiO_2 (19.05 wt.%) and Zr (31,450 ppm or 4.59 wt.% ZrO_2 , or 6.32 wt.% ZrSiO_4). This heavy-mineral subfraction contained more SiO_2 (40.93 wt.%) and Al_2O_3 (16.59 wt.%) than the Buffalo Creek heavy-mineral subfraction (Table 2). The SiO_2 and Al_2O_3 observed in the subfraction was consistent with the quartz, muscovite, and kaolinite observed in the

Jeffersonville Member heavy-mineral subfraction. Only minor amounts of kaolinite were present in the Buffalo Creek heavy-mineral subfraction. The differences in the amounts of quartz, muscovite, and kaolinite were reflected to some extent in the differences in the major element oxides of SiO_2 , Al_2O_3 , and K_2O between the Jeffersonville Member heavy-mineral subfraction and the Buffalo Creek Kaolin Member heavy-mineral subfraction.

The light-mineral subfractions for both the Buffalo Creek Kaolin Member and the Jeffersonville Member contained large amounts of SiO_2 . The Buffalo Creek Kaolin Member light-mineral subfraction had more Al_2O_3 (36.79 wt.%) than the Jeffersonville Member light-mineral subfraction (0.38 wt.% Al_2O_3) (Table 2). The larger Al_2O_3 content reflected a greater presence of kaolinite in the Buffalo Creek light-mineral subfraction. The very large amount of SiO_2 in the Jeffersonville Member light-mineral fraction was consistent with the large amount of quartz observed in that subfraction (Figure 3d). The differences in the weight percentages of both SiO_2 and Al_2O_3 between these two light fractions were consistent with the mineralogy observed in these light fractions. Considerable amounts of tungsten were observed in light-mineral subfractions for both the Buffalo Creek Kaolin Member (8280 mg/kg) and the Jeffersonville Member (5660 mg/kg, Table 3). The large amounts of W in both light-mineral subfractions were attributed to the sorption of large amounts of

Table 2. Major-element analyses (wt.%) of the Buffalo Creek and Jeffersonville Member samples.

Sample	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI	Total
BC CF	42.10	35.43	0.82	0.012	0.06	0.08	0.11	0.21	7.032	0.07	13.39	99.36
JV CF	96.65	0.49	2.00	0.016	0.03	0.05	0.06	0.05	0.168	<0.01	0.28	99.80
BC HF	6.97	3.81	6.27	0.098	0.14	0.15	0.07	0.02	58.28	0.44	ND	
JV HF	40.93	16.59	10.10	0.062	1.38	0.18	0.39	0.45	19.05	0.28	ND	
BC LF	44.82	36.79	0.83	0.007	0.04	0.04	0.15	0.26	0.801	0.03	14.83	98.60
JV LF	95.80	0.38	2.39	0.019	0.01	0.04	0.06	0.05	0.053	<0.01	0.56	99.37
DNC-1 mea ¹	47.14	17.93	9.78	0.150	10.14	11.50	1.88	0.22	0.480	0.07		
DNC-1 mea ²	46.09	18.23	9.98	0.150	9.96	11.23	1.83	0.22	0.480	0.07		
DNC-1 acc	47.15	18.34	9.97	0.150	10.13	11.49	1.89	0.234	0.480	0.07		
W2a mea ¹	52.65	15.36	10.82	0.170	6.39	11.06	2.21	0.63	1.090	0.14		
W2a mea ²	52.76	15.67	10.92	0.170	6.33	11.02	2.21	0.63	1.060	0.15		
W2a acc.	52.4	15.4	10.7	0.163	6.37	10.9	2.14	0.626	1.06	0.13		
SY-4 mea ¹	50.81	21.26	6.26	0.110	0.52	8.01	7.17	1.76	0.300	0.13		
SY-4 mea ²	49.50	19.38	6.07	0.100	0.51	7.97	6.91	1.68	0.280	0.13		
SY-4 acc	49.9	20.69	6.21	0.100	0.54	8.05	7.10	1.66	0.287	0.131		
BIR-1a mea ¹	47.84	15.67	11.39	0.170	9.71	13.61	1.78	0.02	0.980	0.02		
BIR-1a mea ²	48.39	15.66	11.42	0.170	9.68	13.19	1.86	0.02	0.960	0.03		
BIR-1a acc	47.96	15.50	11.30	0.175	9.70	13.30	1.82	0.03	0.960	0.021		

Notes. BC – Buffalo Creek Formation. JV – Jeffersonville Member. mea¹: measured November 16, 2015. mea²: measured December 30, 2015. ND – not determined due to insufficient amount of sample. acc – accepted. LOI – loss on ignition. DNC-1, W2a, BIR-1a, and SY-4 are interlaboratory reference samples (Flanagan and Gottfried, 1980; Flanagan, 1984; Canadian Certified Reference Material). CF – coarse fraction. HF and LF – heavy and light mineral fractions, respectively.

Table 3. Trace-element analyses of Buffalo Creek samples.

Sample	Sc	Be	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	As	Rb	Sr	Y	Zr	Nb
BC CF	87	<1	215	250	4	120	20	60	70	2	6	5	78	273	5778	109
JV CF	1	1	8	8	1	20	10	30	1	1	5	2	7	7	251	8
BC HF	333	<1	1559	1050	5	180	10	190	173	2	50	<2	26	2175	56430	1030
JV HF	68	3	506	390	12	40	60	410	58	3	17	13	172	555	31450	361
BC LF	57	<1	63	150	3	50	20	30	56	1	5	6	6	12	459	15
JV LF	8	<1	8	40	2	<20	<10	<30	<1	1	<5	<2	5	2	72	3
UCC	14	2.1	97	92	17.3	47	28	67	17.5	1.4	4.8	84	320	21	193	12
W2a mea ¹	36	<1	275	90	43	70	110	70	17	1	–	20	191	20	99	–
W2a mea ²	36	<1	270	100	44	70	110	90	18	1	–	–	199	20	93	–
W2a acc	36	1.3	262	92	43	70	110	80	17	1	–	21	190	24	94	–
JR1 mea ¹	–	–	–	–	1	<20	–	–	18	–	16	232	–	–	–	–
JR1 mea ²	–	–	–	–	–	<20	–	–	–	2	–	245	–	–	–	15
JR1 acc	–	–	–	–	0.83	1.67	–	–	16.1	1.88	16.3	257	–	–	–	15.2

Sample	Mo	Ag	In	Sn	Sb	Cs	Ba	Bi	Hf	Ta	W	Tl	Pb	Th	U
BC CF	24	0	0.8	28	1.9	0.5	57	1.1	142	8.4	9	0.1	13	45.5	18.9
JV CF	<2	1.5	<0.2	1	<0.5	<0.5	59	<0.4	6.1	0.4	1	<0.1	<5	1.6	0.7
BC HF	215	–	5.6	215	4.5	<0.5	65	10.8	1380	73.7	52200	<0.1	136	418	152
JV HF	18	–	1.2	35	5.4	<0.5	216	5.6	734	29.1	7070	0.1	89	76.9	56.3
BC LF	4	2	<0.2	6	0.7	<0.5	57	<0.4	12	1.1	8280	<0.1	<5	5.3	2.8
JV LF	<2	<0.5	<0.2	<1	<0.5	<0.5	55	<0.4	1.8	0.2	6550	<0.1	<5	0.4	0.2
UCC	1.1	53	0.056	2.1	0.4	4.9	624	0.16	5.3	0.9	1.9	0.9	17	10.5	2.7
W2a mea ¹	<2	<0.5	–	–	0.90	–	175	<0.4	2.5	–	<1	<0.1	–	2.2	0.5
W2a mea ²	<2	1.0	–	–	–	–	171	<0.4	2.5	–	<1	<0.1	–	2.50	0.6
W2a acc	0.60	0.046	–	–	0.79	–	182	0.03	2.6	–	0.3	0.2	–	2.40	0.530
JR1 mea ¹	–	<0.5	<0.2	3	1.1	22.7	–	0.4	4.5	1.7	–	1.5	19	28.1	9.4
JR1 mea ²	3	1.0	<0.2	3	1.3	19.7	–	0.6	4.2	–	–	1.5	19	24.3	8.5
JR1 acc	3.25	0.031	0.028	2.86	1.19	20.8	–	0.56	4.51	1.86	–	1.56	19.3	26.7	8.88

Notes. All concentrations were recorded as mg/kg. BC: Buffalo Creek Formation. JV: Jeffersonville Member. mea¹: measured November 16, 2015. mea²: measured December 30, 2015. –: not determined. acc: accepted. UCC: Upper Continental Crust. W2a and JR1 are interlaboratory standards (Flanagan and Gottfried, 1980; Imai *et al.*, 1995). CF: coarse fraction. HF and LF denote heavy and light mineral fractions, respectively.

W (0.5–0.8 wt.%) by kaolinite. The concentrations of W in the coarse fractions, not treated with LMT, of the Buffalo Creek (9 mg/kg) and Jeffersonville Member (1mg/kg) were very small (Table 3).

The concentrations of the trace elements of both coarse-fraction samples showed significant enrichments of many trace elements relative to UCC (Rudnick and Gao, 2003). The Buffalo Creek Kaolin Member had both enrichments (V, Cr, Co, Ge, Zr, Nb, Hf, Ta, Th, and U) and depletions (Co, Ba, Sr) of select transition metals (Figure 4a). The Buffalo Creek Kaolin Member heavy-mineral fraction was very enriched (>100 times) in Zr, Nb, and Hf relative to UCC (Figure 4a) and was enriched significantly (10–100 times) in V, Cr, Nb, Ta, Th, and U. The light-mineral subfraction of the Buffalo Creek Kaolin Member was only slightly

enriched (<5 times) relative to UCC for only a few elements: Hf, Ta, Nb, Zr, and Cr. The Jeffersonville Member heavy-mineral fraction was very enriched (>100 times) in Zr and Hf relative to UCC (Figure 4b) and was enriched (5–100 times relative to UCC) in V, Cr, Nb, Ta, U, and Th. The light-mineral subfraction and the coarse fraction of the Jeffersonville Member showed no enrichments of trace elements relative to UCC.

The total REE found in the Buffalo Creek Kaolin Member and Jeffersonville Member coarse (grit) fractions were 583 mg/kg and 25 mg/kg, respectively (Table 4). The lowest total REE (17–97 mg/kg) were found in the light-mineral subfractions. The total REE in the Buffalo Creek heavy-mineral subfraction and the JV heavy-mineral subfraction were 5012 mg/kg and 1647 mg/kg, respectively (Table 4). The heavy-mineral

Table 4. Concentrations of rare-earth elements in Georgia kaolins.

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sc	Y	Σ
BC CF	23.2	48.7	5.72	22.6	6.6	0.8	12.9	3.5	30.1	7.6	25.7	4.12	28.4	4.35	87	273	583
JV CF	2.9	5.2	0.61	2.3	0.5	0.08	1.3	0.2	1.5	0.3	1	0.16	1.1	0.16	1	7	25
BC HC	298	612	72.5	274	75.7	7.64	142	35.4	308	76.7	245	40.7	274	43	333	2175	5012
JV HC	178	312	37.8	133	30.2	5.32	43.7	10	81.8	20.1	65.6	11.3	81.5	13.4	68	555	1647
BC Lt	1.8	3.8	0.44	1.8	0.6	0.11	1.2	0.3	2.8	0.7	2.2	0.37	2.5	0.38	57	12	97
JV Lt	1.3	2.5	0.25	0.9	0.2	0.05	0.2	0.1	0.3	0.1	0.2	0.005	0.3	0.04	8	2	17
UCC	32.3	65.6	6.3	27	4.7	1	4	0.7	3.9	0.83	2.3	0.3	2	0.31	14	21	
C1Ch.	0.4460	1.136	0.1669	0.8279	0.2582	0.0973	0.3300	0.0603	0.3942	0.0889	0.2508	0.0378	0.2479	0.0368	34.2	4.64	
NASC	31.1	66.7	7.70	27.4	5.59	1.18	4.90	0.85	4.17	1.02	2.84	0.48	3.06	0.46			
GASC	84.9	161.2		78.6	15.1	2.7	—	2.7	—	—	—	—	10.5	1.5			
NCSDC 70009 ¹	24.4	61.4	8.2	33.9	13.1	—	15.6	3.2	21.7	4.4	13.8	2.30	15.9	2.38			
NCSDC 70009 ²	25.8	65.3	8.0	33.0	3.0	—	15.0	3.2	21.0	4.4	13.3	2.20	15.9	2.58			
NCSDC 70009 ³	23.7	60.3	7.9	32.9	12.5	—	14.8	3.3	20.7	4.5	13.4	2.20	14.9	2.4			
OREAS 100a ¹	277	499	49.2	158	25.1	3.76	22.3	3.7	23.5	4.9	15.6	2.23	15.4	2.31			
OREAS 100a ²	274	496	50.0	166	26.0	4.07	25.0	4.1	24.4	5.1	16.1	2.40	15.6	2.25			
OREAS 100a ³	260	463	47.1	152	23.6	3.71	23.6	3.80	23.2	4.81	14.9	2.31	14.9	2.26			
OREAS 101a ¹	791	1380	130	402	51.0	8.05	—	5.6	33.5	6.8	20.8	3.00	18.9	2.71			
OREAS 101a ²	844	1520	137	415	52.1	8.45	39.4	5.6	33.7	6.8	—	2.90	19.1	2.69			
OREAS 101 ³	816	1396	134	403	48.8	8.06	43.4	5.92	33.3	6.46	19.5	2.90	17.5	2.66			
JR1 ¹	19.4	43.6	6.10	24.4	6.0	0.27	—	1.0	—	—	—	0.72	4.9	0.74			
JR1 ²	19.7	46.5	5.90	23.4	5.8	0.28	—	0.9	—	0.9	—	0.66	4.7	0.72			
JR1 ³	19.7	47.2	5.58	23.3	6.03	0.30	—	1.01	—	1.02	—	0.67	4.55	0.71			
NCSDC 86318 ¹	1970	426	759	3250	1660	19.1	2240	514	3290	607	1720	277	1860	253			
NCSDC 86318 ²	2040	426	750	3260	1680	19.5	2280	500	3260	602	1700	269	1800	248			
NCSDC 86318 ³	1960	430	740	3430	1720	18.91	2095	470	3220	560	1750	270	1840	260			

Notes: CF – coarse fraction. BC – Buffalo Creek. JV – Jeffersonville Member. HV – heavy mineral subfraction. Lt – light mineral subfraction. Analyses showed good agreement with NCSDC 7009 and OREAS which are interlaboratory standards for geochemical analyses (China National Analysis Center for Iron and Steel, 2008; Ore Research & Exploration Pty Ltd., 2008a, 2008b). Analyses done by Activation Laboratories Ltd., Vancouver, Canada. All analyses in mg/kg.

¹ accepted value. ^{2,3} measured data. UCC: per Rudnick and Gao (2003). C1 Chondrite (C1 Ch.): per Anders and Grevesse (1989). Analyses of interlaboratory standards for Sc and Y are given in Table 3.

fractions also showed the greatest enrichment of the *REE* elements relative to UCC (Figure 5a,b). The heavy-mineral subfractions are also significantly enriched in heavy *REE* (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and Y in both the Buffalo Creek (100 times) and the Jeffersonville Member (50 times) relative to UCC (Figure 5a,b). The Jeffersonville Member and Buffalo Creek Kaolin Member coarse (grit) and heavy fractions are enriched

in the light *REE* (La, Ce, Nd) to a lesser extent than in the *HREE*. The light-mineral fractions are more depleted in the *REE* with the exception of Sc, which showed a significant enrichment relative to other *REE* in both light-mineral subfractions (Figure 5a,b). The *HREE* were enriched by an order of magnitude relative to the *REE* in the Georgia Average Saprolite Composite (Cheshire, 2011).

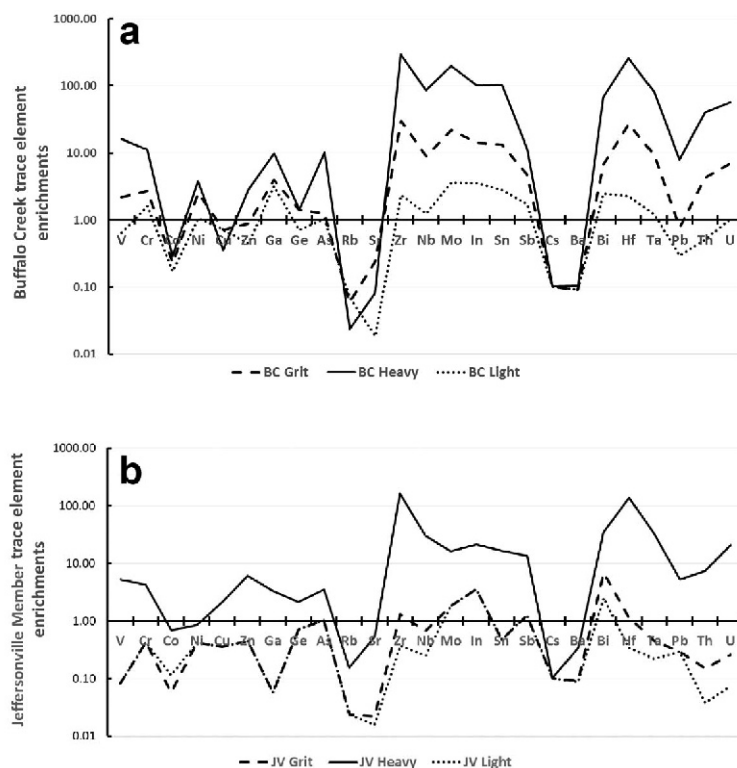


Figure 4. The enrichment/depletions of trace elements in the coarse fractions (grit), heavy-mineral fractions, and light-mineral fraction relative to UCC are shown for (a) the Buffalo Creek Kaolin Member and (b) the Jeffersonville Member.

In terms of the provenance of the *REE*, zircon was considered a likely host for the *REE* given the minerals determined using XRD. The mineralogy predicted using the *MINSQ* calculations showed that phosphate phases were present in small amounts. If zircon is regarded as the primary host of *REE*, then the *REE* possible in the Buffalo Creek are equal to the product of the amount of zircon (11 wt.% zircon, 0.11 g zircon/g heavy subfraction; or 0.110 kg zircon/kg heavy fraction) and the total amount of *REE* possible in zircon (2500 mg *REE*/kg zircon, Hoskin and Schalltegger, 2003). That product, 275 mg of *REE*/kg heavy subfraction, was much less than the 5012 mg of *REE*/kg heavy subfraction observed (Table 4). The trend observed in the *REE* for the heavy-mineral subfraction was modeled by calculating a weighted sum of *REE* in a mixture of 99.5 wt.% zircon, 0.25 wt.% monazite, and 0.25 wt.% xenotime given the amounts of *REE* monazite, xenotime, and zircon (Bea, 1996; Epperson and Elliott, 2018; Figure 6).

In terms of resource evaluation, the amount of *REE* from kaolin ore produced in Georgia was estimated to be 58×10^6 g *REE*/y (58 metric tons (Mt)/y) for the Buffalo Creek Member. This estimate is the product of the mass of discarded kaolin (2.3×10^{12} g/y), the fraction of coarse fraction (0.1 coarse fraction/g of discarded kaolin), the fraction of the heavy-mineral fraction (0.05 g of heavy mineral/g of coarse fraction), and 5012 μ g of *REE*/g of heavy-mineral fraction. This estimate was equal to 0.58%

of the amount of non-Ce imported *REE* compounds (10,000 Mt/y, Gambogi, 2017). This estimate assumed a uniform distribution of the heavy-mineral fraction in mined ore, and known values for the mass of the coarse fractions relative to the total mass discarded. The amount of the coarse fraction ($>44 \mu\text{m}$) was variable within the Georgia kaolins. A significant proportion of the variability depended on the formation being mined. The value of 0.1 g of coarse fraction (*i.e.* grit)/g mined was thought to be a representative value for the amount of coarse fraction in the mined formations of the Georgia kaolins. Similar values (8%) for the fraction of grit (coarse fraction) in the Buffalo Creek and Jeffersonville Members were measured by Dombrowski (1992).

DISCUSSION

Examination by XRD and SEM of the Buffalo Creek Kaolin Member coarse fraction ($>44 \mu\text{m}$) revealed significant amounts of heavy minerals such as zircon and rutile (Table 1; Gardner, 2016). Both rutile and anatase were expected to be present in the heavy-mineral fraction of the Buffalo Creek and other mined formations in the Georgia kaolins (*e.g.* Jeffersonville Member of the Huber Formation, Murray, 1976; Schroeder and Shiflet, 2000).

The Buffalo Creek Kaolin Member coarse fraction and its heavy-mineral subfraction were highly enriched

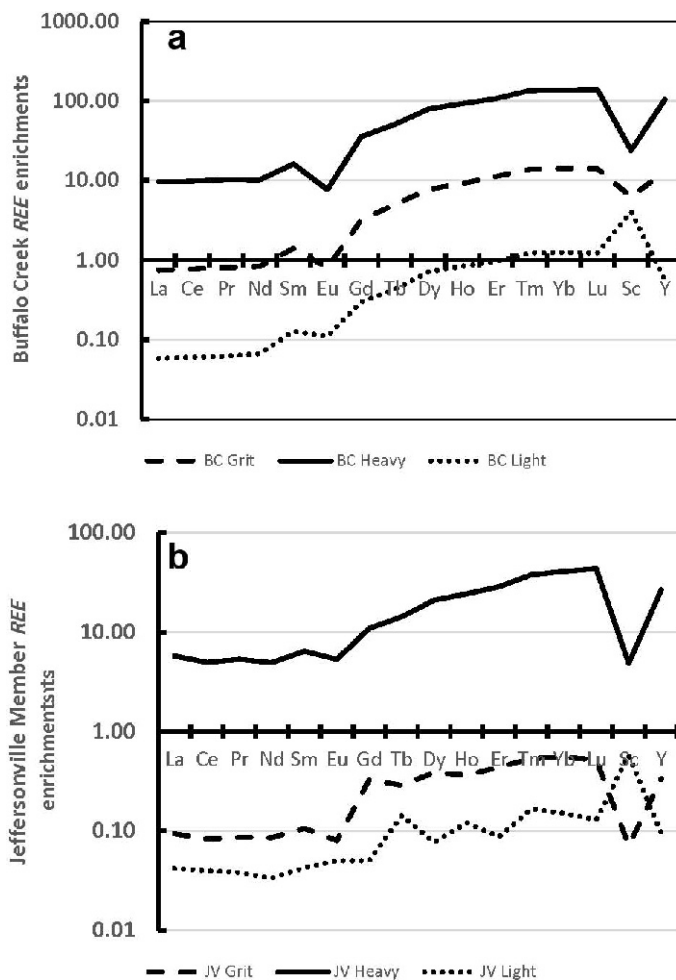


Figure 5. (a) The enrichment/depletions of *REE* in the coarse fractions (grit), heavy-mineral fractions (BC Heavy), and light-mineral fraction (BC Light) relative to UCC are shown for the Buffalo Creek Formation. (b) The enrichment/depletions of *REE* in the coarse fractions (grit), heavy-mineral fractions (JV Heavy), and light-mineral fraction (JV Light) relative to UCC for the Jefferson Member.

in selected transition elements and *REE* relative to UCC. The total concentration of *REE* in the Buffalo Creek heavy-mineral subfraction (5012 mg/kg) may be mineable (Foley and Ayuso, 2015). The *HREE* were especially enriched relative to UCC in the heavy-mineral subfraction. The *REE* signature of the heavy-mineral fraction featuring *HREE* enrichment was similar in shape to the *REE* enrichment signatures for zircon (McLennan, 1989; Watson *et al.*, 2006; Trail *et al.*, 2012). Zircons from continental crustal rocks have variable *REE* contents ranging from 250 to 5000 mg/kg total *REE* (Hoskin and Schaltegger, 2003). The amounts of zircon present in the heavy subfractions were insufficient (6–12%) to account for the amounts of *REE* observed in the heavy-mineral fractions. Xenotime and monazite must be considered as possible sources of *HREE* in the Georgia kaolin samples described in the present study. Coastal Plain sediments of the SE United States are known to contain xenotime and monazite

(Bern *et al.*, 2016). Trace amounts of apatite were observed using XRD (Figures 3a, 3c). A slight increase in P_2O_5 was observed in both heavy-mineral subfractions (Table 2). The increased P could be attributable to the presence of xenotime or monazite in trace amounts. The small amounts of monazite and xenotime (<1%) plus zircon approximated the observed *REE* contents in the Buffalo Creek Kaolin Member heavy-mineral subfraction (Figure 6). The mineral proportions modeled using *MINSQ* showed the presence of small amounts of apatite, monazite, and xenotime in the heavy-mineral subfractions in the present study. Inheritance of the *REE* was a leading hypothesis. Alternatively, the increased P_2O_5 could also have been due to a coupled substitution of P and *REE* for Zr and Si in zircon (Speer, 1982; Hoskin and Schaltegger, 2003).

The sorption of *REE* (and *HREE*) on mineral grains was another plausible explanation advanced to explain the large amounts of *REE* and *HREE* observed in the

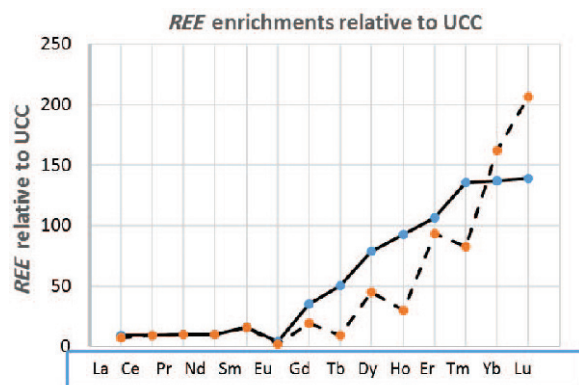


Figure 6. The solid line indicates data from the UCC-normalized *REE* contents for the Buffalo Creek Formation heavy-mineral fraction (same as Figure 5a). The dashed line indicates the UCC-normalized *REE* data of a mixture of xenotime (0.25 wt.%), monazite (0.25 wt.%), and zircon (99.5 wt.%). *REE* data used to construct these mixing curves are from Bea (1996) for xenotime and monazite. Zircon *REE* data are from Mission Placer in SE Georgia (Epperson and Elliott, 2018; reproduced with the permission of Jim Renner).

heavy-mineral subfractions of the kaolin members of Coastal Plain rocks. In this process, the *REE* dissolved from minerals less resistant to weathering (e.g. apatite, Cheshire, 2011) would have precipitated as *LREE*-enriched secondary phosphate minerals such as crandallite, florencite, and gorceixite (Cheshire, 2011). The *HREE*, or *REE* generally, were subsequently sorbed onto phyllosilicate or other mineral phases (e.g. Burkov and Podporina, 1967; Bern *et al.*, 2017). The process envisioned is similar to the presence of *HREE* in mined residual soils (laterites) in SE China. In these laterites, *HREE* were adsorbed preferentially onto mineral surfaces due to their greater charge/size ratios during the weathering processes (Bao and Zhao, 2008 and references therein; Kynicky *et al.*, 2012). An additional source of *REE* related to kaolin-forming processes might be the release of any sorbed *REE* from the microbially aided dissolution of Fe(III) oxides (Shelobolina *et al.*, 1999).

The provenances of the *REE*-bearing minerals such as zircon in the heavy-mineral subfractions and other notable siliclastic minerals are unknown. Large muscovite grains (1–4 cm) found at the base of the Marion Member of the Huber Formation, directly above the top of the Buffalo Creek Member, and in the Buffalo Creek Member, have variable K-Ar and Ar-Ar ages (Elser, 2004). These large muscovite grains displayed discordant Ar-Ar ages ranging from 310 Ma at the edge to as low as 190 Ma in the interior of a large grain (Elser, 2004). Even though these Ar-Ar geochronologic ages were reset by Alleghanian Orogeny metamorphic processes (Kulp and Eckelman, 1961; Smith *et al.*, 1969) and later weathering processes, the presence of large micas is suggestive of erosion from a more proximal

source such as the local igneous intrusions of late Paleozoic age (e.g. Sparta Granite, Figure 1, (299 Ma); Siloam Granite (270 Ma); and Edgefield Granite (255 Ma)) (Jones and Walker, 1973; Fullagar and Butler, 1976; Snoke *et al.*, 1980). The southern mapped extent of the closest igneous body (Sparta Granite) is ~10 miles northeast of the Avant Mines (Figure 1). Alternatively, phyllites (Little River Group) in the Piedmont terrane and phyllites adjacent to the Sparta Granite (Pickering, 1976) were possible sources of coarse mica and other silicate minerals found in the coarse fractions of Georgia kaolins (Dombrowski, 1992; Cheshire, 2011).

The present study does not show as great enrichments of the *LREE* for the Buffalo Creek heavy mineral subfraction as previous studies even though heavy minerals containing both light *REE* (monazite) and heavy *REE* (xenotime) accumulated in the Atlantic Coastal Plain stream and beach placer deposits (Dombrowski, 1992; Cheshire, 2011; Bern *et al.*, 2016). The reasons for the lack of large enrichments of *LREE* in this representative sample of the Buffalo Creek Kaolin Member Kaolins are unclear. The *LREE*-containing minerals in the Georgia kaolins (crandallite and florencite, gorceixite, xenotime, per Cheshire, 2011) would be expected to be present in the heavy-mineral fractions. The most plausible explanation might be that the process producing the coarse mineral grit fraction may have concentrated more of the finer-grained *LREE* phosphate minerals having sizes of 10–20 μm into fractions not studied here (Cheshire, 2011). The origin of the larger P contents in the heavy-mineral subfraction remains an open question.

In the final analysis, the use of lithium metatungstate (LMT) heavy liquid produced a heavy-mineral fraction enriched considerably in the *HREE* and Y as well as some other high field strength (Hf, Zr) elements. Potentially mineable *REE* can be obtained from the application of LMT to the coarse fractions that are already being separated (and discarded) during the typical processing of mined raw kaolin. The *REE* resource is equal to 0.58% of the annual total non-Ce *REE* imported into the USA. This estimated *REE* resource does not include the *LREE* known to exist in the finer fractions of mined kaolin (Dombrowski, 1992; Cheshire, 2011). The concentrations of *REE* observed in the heavy fractions of the Georgia kaolins constitute a novel *REE* (and *HREE*) resource relative to known domestic sources of *REE* (e.g. Long *et al.*, 2016).

CONCLUSIONS

The heavy-mineral subfractions of the coarse fractions (>44 μm ; *i.e.* grit, Murray, 2007) of the Buffalo Creek Kaolin Member and the Jeffersonville Member contain significant enrichment in the *REE*, especially the *HREE*, TiO_2 , and select trace metals (Hf, Zr). The total

REE of the heavy-mineral fractions is 5012 mg/kg (Buffalo Creek) or ~0.50 wt.% *REE*. The total *REE* in the heavy-mineral subfraction of the Jefferson Member is 1648 mg/kg. These total *REE* contents compare favorably with total *REE* contents of mineable resources (e.g. Foley and Ayuso, 2015). The enrichment pattern observed for the heavy-mineral fraction was highly enriched in *HREE* relative to Upper Continental Crust (UCC). The observed enrichment pattern in the *HREE* differs from past work in the Georgia kaolins which showed *LREE* enrichment and the presence of *LREE* phosphate minerals (Dombrowski, 1992; Cheshire, 2011). The difference in the *REE* enrichment pattern was thought at first approximation to be a function of the size fractions being studied between the present study and the earlier two studies. The *HREE* enrichments are consistent with the *HREE* elements being contained in zircon. The amounts of zircon estimated from elemental analyses did not explain the large amounts of the *HREE* observed. The presence of *HREE* in trace amounts of phosphate minerals was not ruled out, given the small increase in P_2O_5 in the heavy-mineral fractions, the trace amounts of apatite inferred from XRD data, the weighted sum of *REE* from small amounts of xenotime and monazite (Figure 6), and the modeled amounts of apatite, xenotime, and monazite from the *MINSQ* calculations. The sorption of released *HREE* on mineral surfaces was also a possible mechanism for accumulation of *HREE*, as is evident in laterites in China (Kynicki *et al.*, 2012).

For the Georgia kaolins, *HREE* and *REE* could, conceivably, be commercial byproducts from the coarse-mineral fractions discarded in the processing of kaolin ore to a kaolin clay product. This grade of *REE* (0.50 wt.%) in the Georgia kaolins pointed to a novel domestic resource for *REE* relative to known domestic sources. This novel resource warrants further examination in light of the lack of new *REE* mining in the USA. In terms of resource evaluation, the amount of *REE* from kaolin ore produced in Georgia was estimated to be 58 Mt/y for the Buffalo Creek. These estimates were equal to ~0.58% of the amount of non-Ce imported *REE* compounds (10,000 Mt/y; Gambogi, 2017). In terms of sediment provenance, the Buffalo Creek coarse fraction is projected to have been weathered from closer Piedmont Province source rocks given its diverse mineral assemblage. These results should stimulate more work to characterize further the *REE* resources and the provenance of these *REE*-containing phases in the Georgia kaolins.

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