

## EARTH'S OLDEST PRESERVED K-BENTONITES IN THE CA. 2.1 Ga FRANCEVILLIAN BASIN, GABON

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**ABSTRACT.** Bentonites are the alteration product of volcanic tephra typically preserved in low-energy, sedimentary environments below baseline. Although volcanic tuffs occur throughout the Earth's history, bentonites older than *ca.* 1.5 Ga have not been described. We present the mineralogy, geochemistry, and age data for K-bentonite beds within the FB Formation in the unmetamorphosed Paleoproterozoic Francevillian Basin, Gabon. The clay mineralogy of the K-bentonites consists predominantly of illite with substantial amounts of kaolinite and trace amounts of long-ordered illite/smectite (R3) mixed layer. The kaolinite content and co-existing 1M and 2M<sub>1</sub> illites are indicative of diagenetic smectite illitization over a prolonged period of time with minimal burial temperature. Their chemical characteristics suggest derivation from calc-alkaline intermediate to felsic magma, related to continental volcanic arc magmatism in a subduction setting. The zircon grains are relatively small, rounded to sub-rounded, and yield <sup>207</sup>Pb/<sup>206</sup>Pb dates that have a narrow range with a weighted mean of 2971 ± 13 Ma, consistent with the age of the underlying crystalline calc-alkaline Archean basement granitoids. This age indicates incorporation of zircons from the Archean basement granitoids into the magma during magmatic activity. Considering that the FB Formation bentonites were derived from a volcanic arc developed along the margin of the West Gabonian block and are preserved in the lower part of the Francevillian Basin, we infer that this basin reflects high-rate, but short-lived sedimentation in a pro-foreland basin setting. Paleogeographically, these K-bentonites could thus serve as a potential correlation marker for the Paleoproterozoic Gabonian and adjacent cratons at *ca.* 2.1 Ga. Based on the current records, these are the world's oldest bentonite beds so far reported.

Keywords: Bentonites, clay mineralogy, U-Pb zircon geochronology, Bulk rock geochemistry, Paleoproterozoic, Francevillian Basin, Gabon

### INTRODUCTION

Bentonites are smectite-dominated clay rocks that are formed by alteration of volcanic ash (tephra/tuff) under the influence of basin fluids and/or *in situ* hydrothermal alteration of pyroclastic rocks (Grim and Güven, 1978; Huff, 2016). Tephra is the explosive volcanic product that is deposited over a relatively short period of time (hours to days) and often found intercalated with sediments in both marine and non-marine realms. The volcanic origin of tephra is often revealed by the presence of primary minerals, including quartz, biotite, zircon, feldspars (commonly sanidine), apatite, monazite, rutile, anatase, and ilmenite (Huff and others, 1996; Huff and others, 1998; Christidis and Huff, 2009; Spears, 2012; Dai and others, 2017). However, in many instances, the primary minerals are altered and the size of fragments decreases with distance from their volcanic source. Because of their metastable nature, volcanic glass and less stable primary minerals in tephra are progressively converted into clay minerals and other secondary products, including zeolites, during alteration. In addition, the abundance, distribution patterns, and ratios of immobile elements such

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as Zr, Ta, Nb, Y, and Rare Earth Elements (REE) have been used widely to trace the composition of the parent magma and infer the tectonomagmatic setting of tephra deposits (Huff and Turkmenoğlu, 1981; Clayton and others, 1996; Huff and others, 1996; Huff and others, 1998; Huff, 2008; Christidis and Huff, 2009; Spears, 2012; Huff, 2016; Dai and others, 2017).

Bentonite, which is a common product in altered tephra, consists predominantly of smectite and other minor clay minerals such as kaolinite, illite, and chlorite. Bentonite beds typically range in thickness from a few millimeters to tens of centimeters depending on the distance from their source, which may not be obvious as it could be several hundreds of kilometers away (Huff and others, 1996; Huff, 2016). Bentonite is transformed into K-bentonite during burial diagenesis and low-grade metamorphism by conversion of smectite into illite via mixed-layer illite-smectite (I/S) with the addition of non-exchangeable  $K^+$  ions (for example, Brusewitz, 1988; Christidis and Huff, 2009; Huff, 2016). The resultant illite-rich beds are called K-bentonites or metabentonites because of the introduction of  $K^+$ , which is commonly derived from potassium-bearing phyllosilicates including K-feldspar and mica during the illitization process. Smectite and illite are the most important clay minerals in K-bentonites, but significant amounts of kaolinite, chlorite, and zeolites can also be formed depending on the alteration conditions (Huff and others, 1996; Huff, 2016; Dai and others, 2017).

Tephra deposits have been widely used as excellent marker beds for stratigraphic correlation and volcanic-event stratigraphy (Saylor and others, 2005), dating sedimentary sequences and refining chronostratigraphic schemes, especially in non-fossiliferous sequences (Su and others, 2008; Sukanuma and others, 2015), and constraining the tectonic and magmatic setting of volcanic rocks (Winchester and Floyd, 1977; Huff and Turkmenoğlu, 1981; Clayton and others, 1996; Huff and others, 1996; Huff and others, 1998; Spears, 2012; Huff, 2016; Dai and others, 2017). Tephra have been formed throughout the whole of Earth history, however, because of their metastable and highly reactive nature, only few occurrences are known from the Precambrian. So far, the oldest reported K-bentonite beds were found in the Mesoproterozoic Belt Supergroup of Montana (Moe and others, 1996) and Xiamaling Formation on North China Craton (Su and others, 2008). Here, we present mineralogy, geochemistry, and zircon age data for the newly-discovered thin, clay-rich K-bentonite beds in the Paleoproterozoic Francevillian Basin with the aim of tracing their mineral evolution, origin, and their implications for the evolution of the Francevillian Basin. Discovery of these K-bentonite beds provides an opportunity to characterize volcanic ash-falls, despite their highly reactive nature, in Paleoproterozoic strata. Their discovery supports the excellent preservation of the Francevillian Basin strata and suggests their deposition in a pro-foreland basin during the early stage of the Nuna (Columbia) supercontinent assembly. These clay-rich K-bentonite beds could thus serve as a potential correlation marker for the Gabonian and adjacent Paleoproterozoic cratons. A K-bentonite of this age is the oldest bentonite deposit that has so far been reported and underlines the continuity and importance of subaerial explosive volcanism in the earlier stage of Earth evolution as well as their preservation potential.

#### THE FRANCEVILLIAN BASIN

The Francevillian Basin is one of the four sub-basins (fig. 1A) that host the extensive Paleoproterozoic Francevillian Group in southeastern Gabon, and is widely known for its natural nuclear reactor at Oklo (Gauthier-Lafaye, 2006), sediment-hosted manganese deposits (LeClerc and Weber, 1980), and megascopic fossil evidence of multicellular life (El Albani and others, 2010, 2014). The geodynamic setting of the Francevillian Group is not well constrained, but it is likely tied to the break-up of an Archean supercontinent and the subsequent 2.2 to 2.0 Ga Eburnean orogeny that formed the West African Central Belt (WCAB) during the Nuna (Columbia) assembly

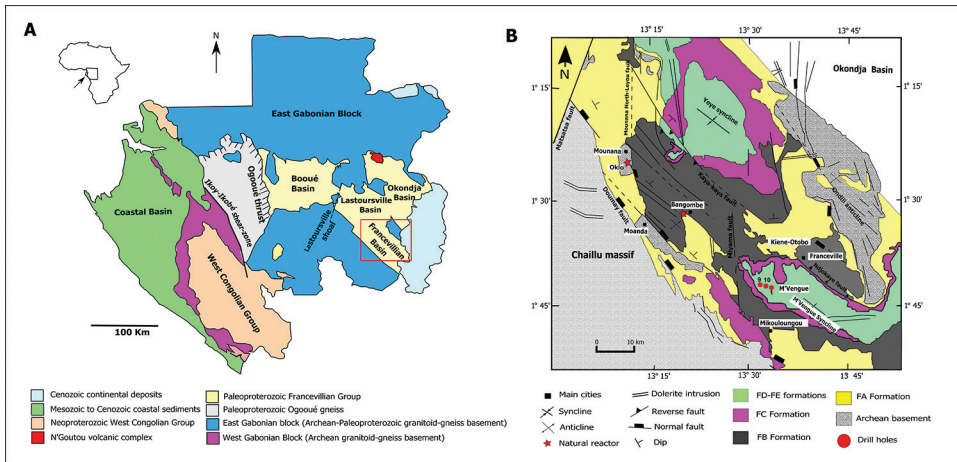


Fig. 1. Geological maps of: (A) Gabon (inset shows Gabon with an arrow on the African continent) and (B) the Paleoproterozoic Francevillian Basin showing locations of the studied drill holes [1 = MVG 1 (1° 43' 46.06" N, 13° 28' 34.57" E); 9 = MVG 9 (1° 43' 34.18" N, 13° 28' 13.58" E); 10 = MVG 10 (1° 43' 40.62" N, 13° 28' 22.51" E)].

(Feybesse and others, 1998; Thiéblemont and others, 2009; Weber and others, 2016). Feybesse and others (1998) and Weber and others (2016) attributed the evolution of the Francevillian Group to three main syn-sedimentary tectonic events: (i) rifting and subsequent break-up of an Archean craton, resulting in a shift from continental to marine deposition, (ii) subduction of the eastern craton under the western craton with ocean closure, and (iii) continental collision resulting in the assembly of the Congo craton along the WCAB.

The Paleoproterozoic Francevillian Group is a sequence of 1.0 to 2.5 km-thick unmetamorphosed siliciclastic to volcanoclastic strata that unconformably overlie the Archean crystalline basement of the Chailu massif, referred to as the East Gabonian block within the Congo craton (fig. 1A; Gauthier-Lafaye and Weber, 1989; Thiéblemont and others, 2009; Weber and others, 2016). The Francevillian Group strata have been divided into five lithostratigraphic formations (FA to FE) in the Francevillian and Okondja basins (figs. 1B and 2; Weber, ms, 1968). The Archean basement is composed of calc-alkaline gneisses, granitoids, and greenstones that were emplaced during two major magmatic events at 2928 to 2870 Ma and 2800 to 2500 Ma (Caen-Vachette and others, 1988; Bouton and others, 2009; Thiéblemont and others, 2009). The FA Formation rests directly on the Archean basement and predominantly consists of fluvial to fluvio-deltaic, coarse- to fine-grained sandstones and conglomeratic sandstones with minor interlayered mudstones (Haubensack, ms, 1981; Gauthier-Lafaye and Weber, 1989; Bankole and others, 2015).

The predominantly marine FB Formation, within which the clay-rich K-bentonite beds are found, has been subdivided into FB1 (a, b, and c) and FB2 (a and b) members based on lithological variations (fig. 2). The FB1a and FB1b units are dominated by fine-grained black shales and siltstones alternating with interbedded medium- to coarse-grained sandstones, breccias, and conglomerates in an upward-fining sequence. The FB1c unit is mainly composed of black shales with interlayered thin iron-rich sediments and a thick manganese ore deposit at the top. The FB2a unit is essentially composed of massive sandstone with thin interlayered black shale observed in few outcrops and it is sharply overlain by the FB2b unit, which is composed of black shales interbedded with thin layers of siltstones. The FB Formation is generally interpreted to

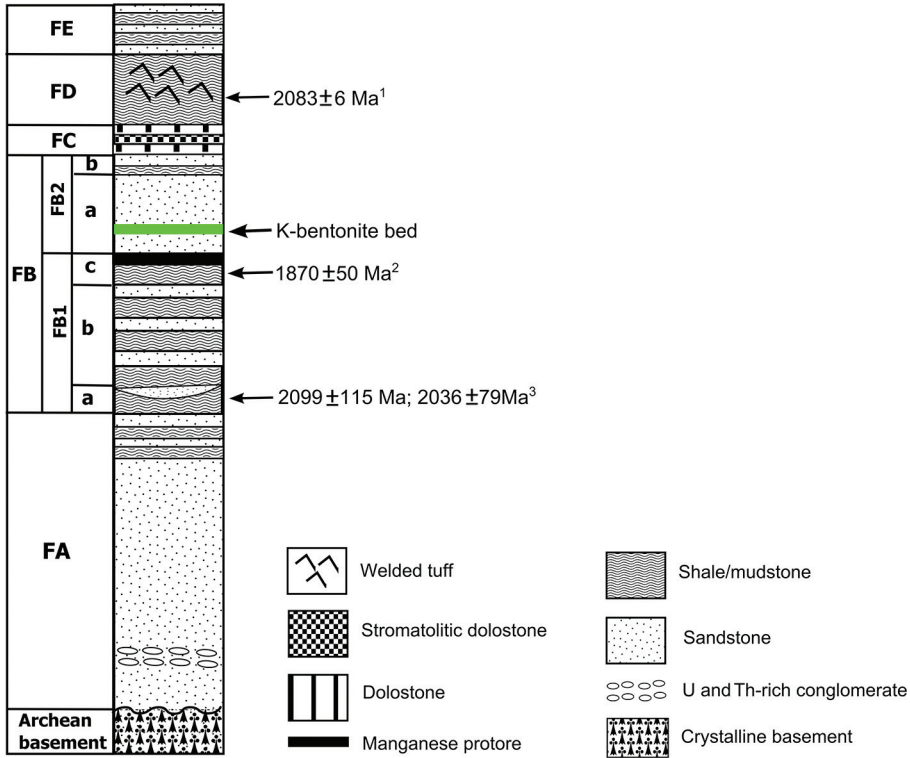


Fig. 2. Lithostratigraphic column of the Francevillian Group showing the stratigraphic position of the K-bentonite beds (modified from Weber, ms, 1968) (<sup>1</sup> Horie and others, 2005; <sup>2</sup> Bonhomme and others, 1982; <sup>3</sup> Bros and others, 1992).

have formed during extension and subsidence in the Francevillian Basin and it is absent in the western Bououé Basin. The FB deposition was accompanied by intrusion of alkaline granite and syenite (the N’Goutou Complex), in the northern part of the Okondja Basin (see fig. 1A; Gauthier-Lafaye and Weber, 2003; Thiéblemont and others, 2009, 2014) and emplacement of alkaline volcanic lavas including basalts and trachytes (Thiéblemont and others, 2014) in the basal part of the formation. The overlying FC Formation is a shallow-marine deposit consisting of massive dolostone and thick-banded stromatolitic cherts with thin black shale layers (Weber, ms, 1968; Gauthier-Lafaye and Weber, 2003; Prétat and others, 2011). The FD Formation was deposited in a shallow-marine environment and is dominantly composed of black shales with thin, interbedded fine- to medium-grained sandstones and volcanic tuffs throughout the whole formation (Gauthier-Lafaye and Weber, 1989, 2003; Thiéblemont and others, 2009, 2014). The topmost FE Formation consists of epiclastic fine- to medium-grained sandstones with interlayered shales (Gauthier-Lafaye and Weber, 1989, 2003; Thiéblemont and others, 2014). Overall, basin-scale stratigraphic correlation of the Francevillian Group strata appears to be very difficult due to the lateral facies changes and thickness variations and complex tectonic activity during deposition of the Francevillian Group.

Attempts to directly date deposition of the Francevillian Group strata have so far been inconclusive. The timing of early diagenesis in the FB1b unit is constrained by the Sm-Nd isotopic ages of 2099 ± 115 Ma and 2036 ± 79 Ma from the <0.4 μm and <0.2

$\mu\text{m}$  clay fractions, respectively, in the Francevillian Basin (Bros and others, 1992). Dating of  $<1.5 \mu\text{m}$  and  $<2.0 \mu\text{m}$  authigenic illites from the FB1c unit (fig. 1B) gave an apparent Rb-Sr isochron date of  $1870 \pm 50 \text{ Ma}$  for late diagenesis in the Francevillian Basin (Bonhomme and others, 1982). Horie and others (2005) obtained a SHRIMP U-Pb zircon age of  $2083 \pm 6 \text{ Ma}$  for ignimbrite in the FD Formation; however the data for this age have not yet been published. The N’Goutou Complex that intrudes the FA and FB formations in the Okondja Basin (see fig. 1A) was imprecisely dated at  $2027 \pm 55 \text{ Ma}$  using an upper intercept for discordant TIMS U-Pb zircon data (Moussavou and Edou-Minko, 2006). Consistent with these ages, the FB and FC formations, based on  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  trends, are considered to record the end of the 2.22 to 2.06 Ga Lomagundi carbon isotope excursion and to be correlative with the Zaonega Formation in the Onega basin of Karelia, Russia (Kump and others, 2011), which is also imprecisely dated (Ovchinnikova and others, 2007; Martin and others, 2015). The end of the Lomagundi carbon isotope excursion has been bracketed elsewhere in Fennoscandia between 2.11 and 2.06 Ga (Karhu and Holland, 1996; Martin and others, 2013). Combined, these age constraints place the age of deposition for the Francevillian Group close to 2.11 to 2.06 Ga. However, three recent studies challenge this interpretation. First, Martin and others (2015) argued that the Zaonega Formation of Karelia, Russia, which was considered to record the end of the Lomagundi carbon isotope excursion and has been correlated to the FB and FC formations of the Francevillian Group, is much younger at *ca.* 1980 Ma. This interpretation however hinges on the geological position of the dated material, specifically, whether it was derived from a volcanic flow or an intrusive sill, which has not yet been resolved (see Bekker and others, 2016 for further discussion). Secondly, Bekker and others (2016) reported on a short-term, positive C isotope excursion at *ca.* 2.03 Ga. This discovery allows for positive perturbations in the global carbon cycle younger than the Lomagundi carbon isotope excursion. However, available age constraints for the Francevillian Group argue strongly against a *ca.* 2.03 Ga age. Finally, Sawaki and others (2017) published a new MC-ICP-MS  $^{207}\text{Pb}$ - $^{206}\text{Pb}$  zircon age for the N’Goutou Complex ( $2191 \pm 12 \text{ Ma}$ ), which, if correct, would shift the depositional age of the Francevillian Group to the beginning of the Lomagundi carbon isotope excursion. However, the authors also recognized the complex nature of the dated zircons and their highly discordant ages. In summary, the age for the end of the Lomagundi carbon isotope excursion, *ca.* 2.11 to 2.06 Ga, currently provides the best estimate for the depositional age of the Francevillian Group.

#### SAMPLES AND METHODS

*Samples.*—In this study, seven clay-rich samples from the FB Formation were collected from 3 drill cores near M’Vengue (MVG 1, MVG 9, and MVG 10; figs. 1B and 3A), in the central part of the Francevillian Basin (fig. 1B). These materials are poorly lithified, and occur as sharply bounded, interbedded thin beds with intercalated sandstones and of variable thickness, ranging from  $<40 \text{ cm}$  to  $\sim 90 \text{ cm}$  (figs. 3A and 3B) in the basal part of the FB2a unit, close to the transition between the FB1c and FB2a units (fig. 2). Two clay-rich beds were identified in the MVG 1 drill-hole, while only one bed was identified in both the MVG 9 and MVG 10 drill cores. Most of the samples are light-green (MVG 1\_7.2, MVG 1\_7.4, MVG 1\_7.6, MVG 1\_12.5, and MVG 9\_13), whereas two samples are light red and sandy (MVG 1\_11.6 and MVG 10\_35).

*Mineralogy and petrography.*—The mineralogy of the selected samples was examined by X-ray diffraction (XRD) on bulk powders and clay-size fractions using a Bruker D8 ADVANCE diffractometer ( $\text{CuK}\alpha$  radiation) with operating conditions of 40 kV, 40 mA, and 0.025/s step size. The powdered bulk-rock samples were examined over the  $2^\circ$ - $65^\circ$   $2\theta$  angular range. For the clay-mineral fractions, the samples were first ultrasonically-dispersed in distilled water to liberate the fine fraction without any chemical treatment.

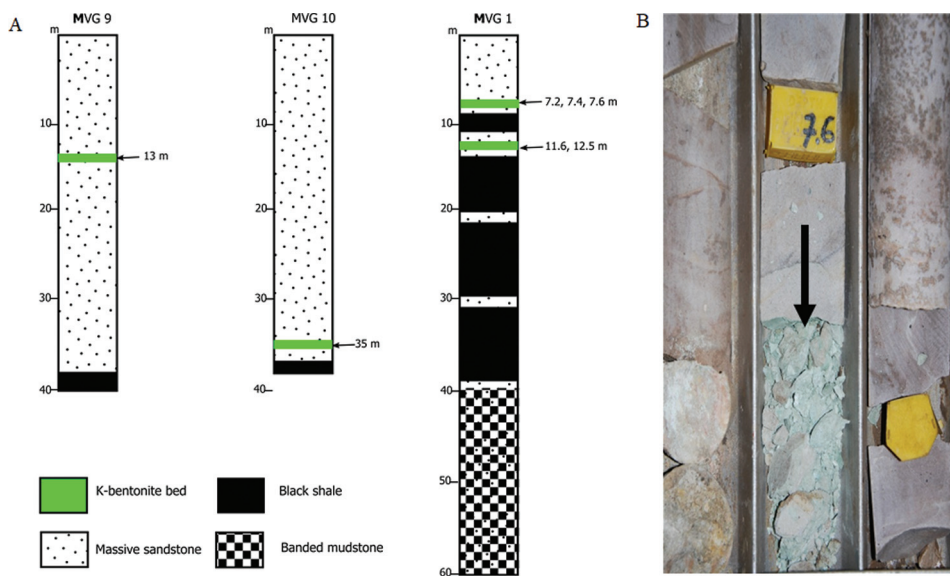


Fig. 3. (A) Schematic log sections of the sampled drill holes showing the stratigraphic positions of the K-bentonite samples; (B) MVG 1 drill hole showing a green K-bentonite bed (black arrow) within sandstones.

The clay-size fraction was separated by sedimentation and program-timed centrifugation (Moore and Reynolds, 1997). Oriented mounts of the  $<1 \mu\text{m}$  and  $<2 \mu\text{m}$  fractions were prepared by sedimentation on glass slides and analyzed after air-drying overnight at room temperature (AD), ethylene-glycol solvation (EG), and Ca-saturation and heating to  $350^\circ\text{C}$  for 4h. The oriented mounts were scanned from  $2^\circ$  to  $35^\circ 2\theta$  angular range for AD and  $2^\circ$  to  $30^\circ 2\theta$  for EG and heat treated preparations. Identification of minerals is based on the mineral principal peak positions and comparison with International Centre for Diffraction Data (ICDD) files (Brindley and Brown, 1980; Moore and Reynolds, 1997). Illite polytypes were determined from analysis of the  $<1 \mu\text{m}$  and  $<2 \mu\text{m}$  random powder mounts from  $19^\circ$  to  $34^\circ 2\theta$  angular range. The proportion of the  $1M$  and  $2M_1$  illite polytypes was estimated using the method described by Grathoff and Moore (1996). In addition, coarse grains including the heavy mineral fraction were isolated by ultrasonification and sedimentation until clay free. The extracted coarse-grained fraction was analyzed with XRD and scanning electron microscope (SEM). In addition, polished thin sections of samples were prepared parallel and perpendicular to bedding. Thin sections and small sample chips were carbon coated and examined at the University of Poitiers, France with a JEOL JSM 6400 SEM equipped with energy-dispersive detector (EDS), in back-scattered electron (BSE) imaging mode.

*Whole-rock geochemistry.*—Bulk-rock chemical analyses of four samples were performed on dried and powdered samples at the *Service d'Analyse des Roches et des Minéraux* (SARM-CRPG) in Nancy, France. Major elements were analyzed using inductively-coupled plasma atomic emission spectrometry (ICP-AES) and trace elements, including REE, were analyzed using inductively-coupled plasma mass spectrometry (ICP-MS).

*Zircon dating.*—*In situ* U-Pb isotopic data were obtained by laser-ablation inductively coupled plasma spectrometry (LA-ICP-MS) on thin sections at *Laboratoire Magmas & Volcans* in Clermont-Ferrand, France. The analyses involved ablation of zircons with a Resonetics M-50 laser system operating at a wavelength of 193 nm coupled to an

Agilent 7500 cs ICP-MS equipped with a dual pumping system to enhance sensitivity (Paquette and others, 2014). Operational conditions were spot diameter of 15  $\mu\text{m}$ , repetition rate of 3 Hz, and a laser fluence of 4 J/cm<sup>2</sup>. The analytical method for isotope dating is similar to that developed and reported by Hurai and others (2010). Data were corrected for U-Pb fractionation occurring during laser ablation and for instrumental mass discrimination by standard bracketing with repeated measurements of the GJ-1 zircon reference material (Jackson and others, 2004). The 91500 zircon reference material (Wiedenbeck and others, 1995) was used as an internal standard. Occurrence of common Pb in the sample was monitored by the evolution of the <sup>204</sup>(Pb+Hg) signal intensity, but no common Pb correction was applied owing to the large isobaric interference from Hg. The <sup>235</sup>U signal was calculated from <sup>238</sup>U on the basis of the ratio <sup>238</sup>U/<sup>235</sup>U = 137.88. Data reduction was carried out with the software package GLITTER<sup>®</sup> from Macquarie Research Ltd. (van Achterbergh and others, 2001). Calculated isotopic ratios were exported and plotted on a concordia diagram with Isoplot/Ex v. 2.49 (Ludwig, 2001).

## RESULTS

### *Mineral Composition*

Detailed mineralogical study has been carried out on the selected samples (figs. 4, 5, 6). Mineralogical data show that the samples are clay-rich and contain a variety of non-clay minerals including quartz, zircon, anatase, biotite, and monazite that are suspended in the clay mineral matrix (figs. 4 and 5). Quartz is the most abundant non-clay mineral, occurring mostly as sub-angular grains of various sizes (fig. 4A). The zircon crystals are generally small (figs. 4B and 4C) with rare larger grains (fig. 4D), sub-rounded to rounded with corroded edges (fig. 4D), and maybe cracked and broken (fig. 4B), suggesting inheritance. Compared to zircon, anatase grains are much smaller in size and occur in lesser amounts (fig. 4C). Biotite occurs as individual elongated brownish flakes (fig. 4E) while the monazite grains are mostly broken and pitted (fig. 4F).

The <1  $\mu\text{m}$  and <2  $\mu\text{m}$  clay-size fraction shows that the samples contain mostly illite and/or mica with associated kaolinite (figs. 6 and A-1). The illite peaks are sharp and do not shift in Ca-saturated slides, but are slightly modified in slides treated with ethylene glycol (EG) and heated to 350 °C (fig. 6). Asymmetric peaks at  $\sim 10$  Å, typical for illite, indicate the presence of expandable I/S mineral. Decomposed (001) illite peaks in the EG patterns reveal the presence of well-crystallized illite (WCI), poor-crystallized illite, and long-range ordered R3 I/S with  $\sim 5$  percent expandable layer (figs. 7A, 7B, and A-2). Kaolinite is identified by its 001 and 002 diagnostic peaks at 7.15 Å and 3.57 Å, respectively. Comparison of diagnostic peaks for illite polytypes (Moore and Reynolds, 1997) generated with <1  $\mu\text{m}$  and <2  $\mu\text{m}$  random powder mounts shows that the illite is composed of a mixture of 1M and 2M<sub>1</sub> illite polytypes (fig. 8). No significant variation in illite polytypes with size fraction was observed in the analyzed samples. The ratios of 1M to 2M<sub>1</sub> polytypes in the <1  $\mu\text{m}$  fraction are 0.90, 1.20, and 1.98 for the MVG 1\_7.2, MVG 9\_13, and MVG 10\_35 samples, respectively.

### *Chemical Composition*

The SiO<sub>2</sub> content of the K-bentonites ranges from 51.78 to 58.50 percent for the finer MVG 1\_7.6 and MVG 9\_13 samples and 79.18 to 85.73 percent for the coarser-grained MVG 1\_12.5 and MVG 10\_35 samples (table 1). SiO<sub>2</sub> inversely varies with Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, TiO<sub>2</sub>, and K<sub>2</sub>O contents (fig. 9). In contrast, Fe<sub>2</sub>O<sub>3</sub>, MgO, TiO<sub>2</sub>, and K<sub>2</sub>O show positive correlation with Al<sub>2</sub>O<sub>3</sub> concentration, indicating their control by the abundance of phyllosilicates (clay minerals). The data plot along the illite-kaolinite end-member mixing line on the 4Si-M<sup>+</sup>-R<sup>2+</sup> plot, suggesting that both clay minerals formed during diagenesis and are consistent with a highly illite-rich I/S

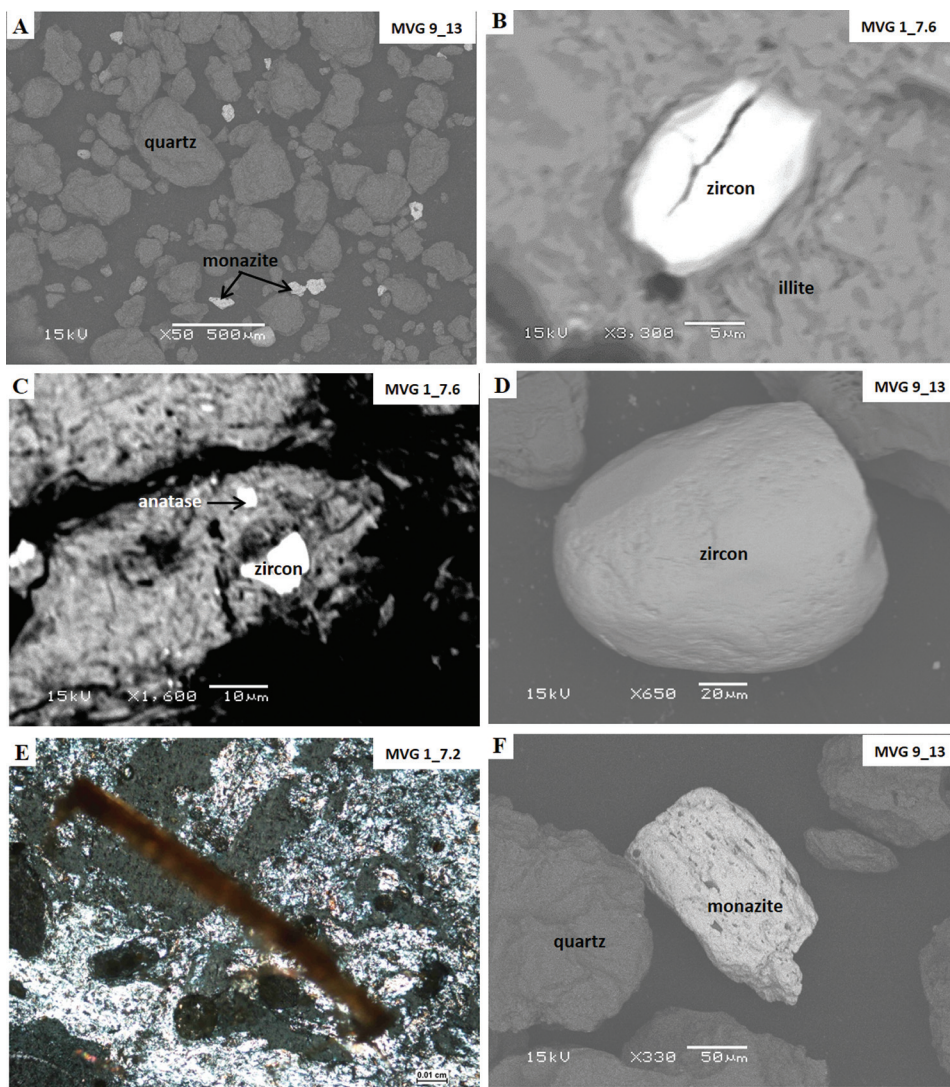


Fig. 4. Micrographs showing examples of the primary mineral grains in the K-bentonite beds of the Paleoproterozoic Francevillian Basin in backscattered scanning electron microscope mode (A, B, C, D, and F) and cross-polarized light (E): (A) quartz and monazite grains in separated coarse-grained fraction; (B) cracked subhedral zircon crystal in illite matrix (thin section); (C) small anatase and zircon crystals in clay mineral matrix (thin section); (D) sub-rounded zircon crystal in separated coarse-grained fraction; (E) elongated, altered biotite grain (thin section); (F) broken and rectangular monazite crystal in separated coarse-grained fraction.

minerals (Meunier and Velde, 2004; fig. 10). CaO and Na<sub>2</sub>O are extremely low, ranging from 0.00 to 0.04 and 0.00 to 0.07 percent, respectively, reflecting the absence of carbonates and feldspars.

The trace element and REE data are reported in table 1. All the samples display similar primitive mantle-normalized trace element (fig. 11) and chondrite-normalized REE (fig. 12) patterns. They are characterized by enrichment in large-ion lithophile elements (LILE: Cs, Rb, Ba, and K) relative to the high-field strength elements (HFSEs:

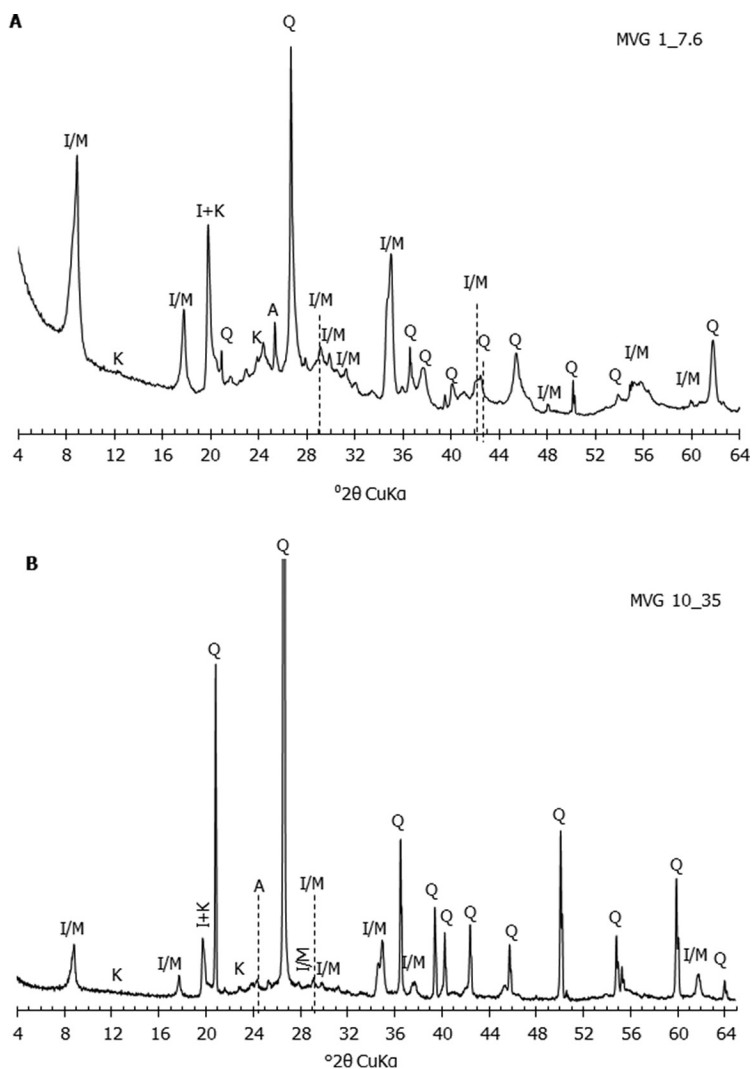


Fig. 5. X-ray diffraction (XRD) patterns of bulk-sample powders of K-bentonites from the Francevillian Basin: (A) MVG 1\_7.6; (B) MVG 10\_35. I/M = illite/mica; K = kaolinite; Q = quartz; A = anatase.

Y, Zr, Hf, Nb, Ta, and Ti), Ti-Ta-Nb troughs, strongly depleted Sr (fig. 11), and relatively high Th/U ratios between 5.13 and 15.30 (table 1). They all show enrichment in Hf and Zr relative to Ti, indicating the predominance of zircon over Ti-bearing minerals. All samples exhibit REE trends with overall moderate enrichment in light REEs (LREEs) [ $(\text{La}/\text{Yb})_{\text{N}} = 8.69\text{--}28.20$ ], relatively flat heavy REE (HREE) [ $(\text{Gd}/\text{Yb})_{\text{N}} = 1.23\text{--}2.85$ ], and weak negative Eu anomalies [ $\text{Eu}/\text{Eu}^* = \text{Eu}_{\text{N}}/(\text{Sm}_{\text{N}} \cdot \text{Gd}_{\text{N}})^{1/2} = 0.80\text{--}0.89$ ] (fig. 12). REE concentrations decrease with increasing  $\text{SiO}_2$  content, reflecting quartz dilution.

#### *U-Pb Zircon Geochronology*

U-Pb dates from 31 analytical spots on zircon crystals yield an upper concordia intercept at  $2962 \pm 16$  Ma (fig. 13), omitting 2 outliers. The analyses range from

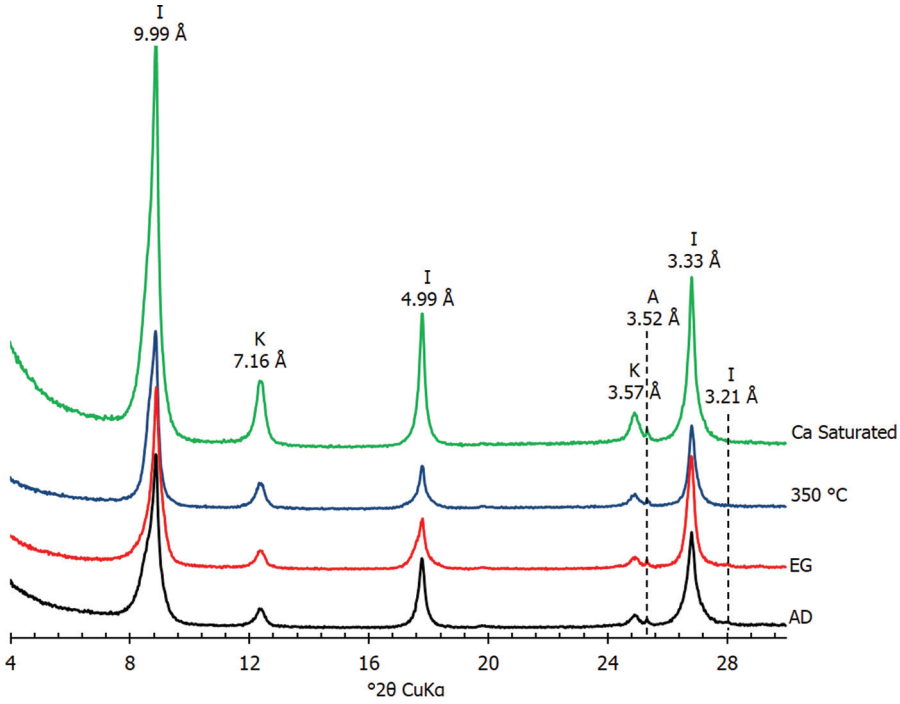


Fig. 6. Representative X-ray diffraction (XRD) patterns of oriented, <2 μm clay fraction in air-dried (AD), ethylene glycol-saturated (EG), heated to 350 °C, and calcium-saturated (Ca-saturated) preparations for the sample MVG 1\_7.2. I = illite; K = kaolinite; Q = quartz; A = anatase.

concordant to 83 percent discordant with the most discordant grains displaying the highest U and Th contents. The <sup>207</sup>Pb/<sup>206</sup>Pb ages are consistent with a weighted mean of 2971 ± 13 Ma (MSWD = 1.0). We interpret the zircon crystallization age as 2962 ± 16 Ma. Their variable Th/U ratios between 0.3 and 4.9 (table 2), with a relatively high mean value of 1.78, are indicative of a magmatic origin and not the result of metamorphic overprinting (Paquette and Mergoïl-Daniel, 2009; Hurai and others, 2010). Given the discordia passes close to the origin, the Pb loss and high contents of U and Th of the ca. 3 Ga zircons (contributing over a long time to the metamictization of zircon lattice) likely suggests a recent event that is related to fluid ingress.

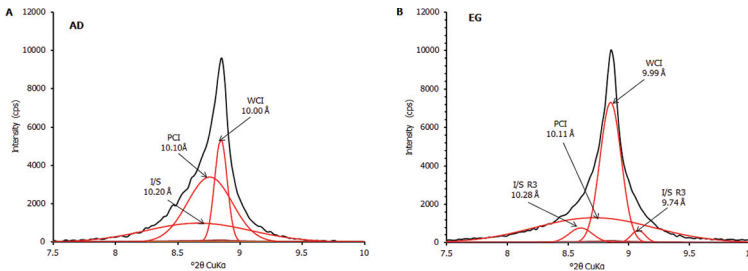


Fig. 7. Decomposed 001 illite peaks of <1 μm clay fraction in (A) air-dried (AD) and (B) ethylene glycolated (EG) preparations for sample MVG 9\_13. WCI = well-crystallized illite; PCI = poorly crystallized illite; I-S = illite-smectite mixed-layer clay minerals.

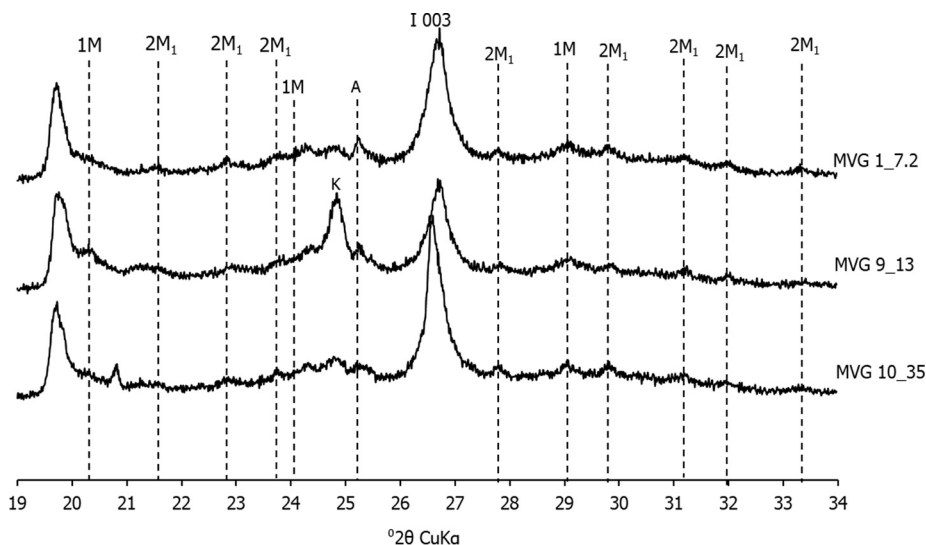


Fig. 8. XRD patterns of  $<1 \mu\text{m}$  random powder showing signature of illite polytypes in 3 samples of the M'Vengue K-bentonites, Francevillian Basin, Gabon. I = illite; 1M and 2M<sub>1</sub> = illite polytypes; A = anatase; K = kaolinite.

## DISCUSSION

### Mineralogy

Mineralogy and chemical composition of the olive-green to light-red, clay-rich thin beds within the FB2 member of the Francevillian Basin demonstrate that they are K-bentonites. They have sharp contacts with the basal sandstones, suggesting rapid change in the depositional environment. The predominance of illite, trace amounts of mixed-layer I/S minerals, significant amounts of kaolinite, and the nature of illite polytypes are all characteristic of K-bentonites formed by kinetically controlled, prolonged smectite illitization at low temperature (Velde and Vasseur, 1992). The absence of smectite in the samples does not imply that it was never present, but rather reflects an advanced stage of smectite illitization. K-feldspar, which is the main source of  $\text{K}^+$  for smectite illitization process, is completely absent in the studied samples, suggesting diffusion of potassium derived from dissolution of K-bearing minerals in adjacent lithologies into the bentonites (Huff and Turkmenoğlu, 1981; Bruswitz, 1988; Stille and others, 1993). Considering the age of the Francevillian Group, one would expect the predominance of 2M<sub>1</sub> over 1M polytype in such old rocks, but our observations suggest otherwise as 1M polytype appears to be as abundant as 2M<sub>1</sub> polytype in the K-bentonites (fig. 8). Therefore, the coexistence in equal amounts of 2M<sub>1</sub> and 1M illite polytypes, which are the ultimate products of smectite alteration in diagenetic smectite-to-illite reaction, cannot be explained by low-grade metamorphic conditions or inheritance of detrital mica, but rather indicates prolonged recrystallization, which is consistent with the age of the succession. Kaolinite in altered volcanic ash is mainly an authigenic product of altered biotite, feldspars, amphiboles, and pyroxenes (Dai and others, 2017). Kaolinite is unstable at higher diagenetic temperatures where it is replaced by either illite or chlorite. Although, we could not identify the precursor mineral for kaolinite in this study, its preservation in substantial amounts in the Francevillian Basin K-bentonites constrains the alteration process to relatively low temperatures and shallow depths.

TABLE 1

*Bulk major and trace element compositions of four K-bentonite samples from the Francevillian Basin, Gabon*

Sample	MVG1_7.6	MVG 9_13	MVG 10_35	MVG 1_12.5
Major elements (%)				
S <sub>2</sub>	51iO.78	58.50	85.73	79.18
Al <sub>2</sub> O <sub>3</sub>	28.76	25.46	7.83	12.54
Fe <sub>2</sub> O <sub>3</sub>	0.88	0.59	0.39	0.36
MnO	0.00	N.D. <sup>†</sup>	N.D. <sup>†</sup>	N.D. <sup>†</sup>
MgO	1.83	1.14	0.49	0.85
CaO	0.04	N.D. <sup>†</sup>	N.D. <sup>†</sup>	N.D. <sup>†</sup>
Na <sub>2</sub> O	0.07	0.04	N.D.	N.D.
K <sub>2</sub> O	8.62	5.82	2.37	3.36
TiO <sub>2</sub>	0.72	0.63	0.13	0.43
P <sub>2</sub> O <sub>5</sub>	0.11	N.D. <sup>†</sup>	N.D. <sup>†</sup>	N.D. <sup>†</sup>
LOI <sup>*</sup>	6.53	6.62	1.84	3.31
Total	99.35	98.79	98.78	100.3
Trace elements (ppm)				
As	N.D. <sup>†</sup>	4.31	0.47	0.22
Ba	1739	1470.85	630.87	715.40
Be	2.547	1.53	0.43	1.14
Bi	0.5	0.26	0.18	0.20
Cd	0.33	0.26	0.04	0.06
Ce	141.2	67.47	9.91	96.93
Co	1.51	1.09	0.38	0.45
Cr	3302	3359.61	46.85	62.37
Cs	11.14	3.61	1.50	4.32
Cu	17.72	8.71	N.D. <sup>†</sup>	N.D. <sup>†</sup>
Dy	4.57	2.12	0.43	2.63
Er	2.04	1.36	0.34	1.42
Eu	2.10	0.88	0.12	1.25
Ga	39.55	20.43	8.96	15.77
Gd	6.94	2.54	0.35	3.85
Ge	1.57	1.23	0.72	1.02
Hf	11.8	19.01	2.84	6.17
Ho	0.76	0.45	0.11	0.52
In	0.11	0.04	0.02	0.03
La	71.43	45.32	4.91	54.31
Lu	0.30	0.25	0.06	0.20
Mo	N.D. <sup>†</sup>	N.D. <sup>†</sup>	N.D. <sup>†</sup>	N.D. <sup>†</sup>
Nb	11.14	8.99	1.82	6.46
Nd	55.38	31.10	3.46	34.73
Ni	27.08	23.15	11.24	11.94
Pb	18.87	5.07	1.15	33.75
Pr	15.44	9.08	0.98	10.12
Rb	218.9	144.41	52.70	88.93
Sc	11.81	11.67	3.07	5.39
Sb	0.248	0.20	0.15	0.12
Sm	9.266	4.18	0.51	5.26
Sn	1.9	N.D. <sup>†</sup>	N.D. <sup>†</sup>	N.D. <sup>†</sup>
Sr	92.72	19.14	2.42	25.58
Ta	0.97	0.75	0.16	0.55
Tb	0.90	0.35	0.06	0.48
Th	26.72	15.02	3.34	13.45
Tm	0.30	0.22	0.05	0.20
U	1.75	2.92	0.33	2.55
V	131.8	65.91	22.99	45.28
W	20.98	13.77	1.95	2.24
Y	24.51	13.28	3.86	17.64
Yb	1.96	1.61	0.38	1.31
Zn	55.03	37.62	8.98	13.79

Note: \* LOI = Loss on ignition; <sup>†</sup> N.D. = not detected.

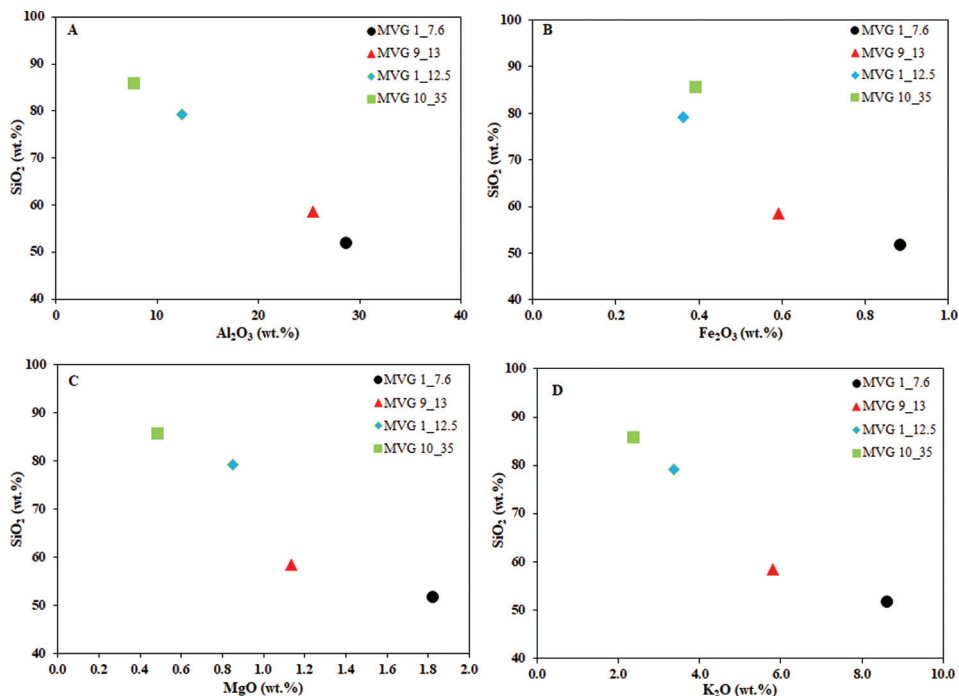


Fig. 9. Whole-rock elemental bivariate plots of SiO<sub>2</sub> versus selected major element oxides for the K-bentonites from the Paleoproterozoic Francevillian Basin, Gabon: (A) SiO<sub>2</sub> vs. Al<sub>2</sub>O<sub>3</sub>; (B) SiO<sub>2</sub> vs. Fe<sub>2</sub>O<sub>3</sub>; (C) SiO<sub>2</sub> vs. MgO; (D) SiO<sub>2</sub> vs. K<sub>2</sub>O.

Clay mineralogy of the K-bentonites is similar to that of the other described Precambrian K-bentonites (Moe and others, 1996) and is remarkably different from that of the surrounding FB Formation shales and sandstones. The FB2b and FB1c units black shales and sandstones contain randomly and regularly ordered I/S minerals, chlorite, 1M<sub>d</sub>/1M<sub>1</sub> illite polytypes, and non-clay minerals including quartz, plagioclase, muscovite, pyrite, and dolomite (Bros and others, 1992; Ossa Ossa and others, 2013; Ngombi-Pemba and others, 2014). Notably, these are the only known Precambrian shales with preserved smectite-rich, randomly ordered I/S minerals. Ossa Ossa and others (2013) attributed survival of I/S minerals to sluggish illitization in the presence of abundant organic matter; Ngombi-Pemba and others (2014) argued that their presence was due to incomplete illitization related to low-K content of the FB Formation lithologies. We consider that the difference in mineral composition between the K-bentonites and adjacent shales likely reflects different source composition, depositional conditions, and, consequently, post-depositional alteration pathways.

Spears (2012) suggested that small rounded to sub-rounded zircon grains in volcanic ash are due to either magmatic processes before ash eruption or to transport in the ash cloud, while studies such as by Guerra-Sommer and others (2008) and Huff and others (1997) proposed that large rounded zircon grains in volcanic ash indicate inheritance from the basement. Zircon grains in the Francevillian Basin K-bentonites vary in size and are mostly rounded with the ages similar to those of the underlying Mesoproterozoic calc-alkaline granitoids ( $2928 \pm 6$  Ma; Thiéblemont and others, 2009), and older than the constrained depositional age of the FB Formation where they are found. Combined, these observations clearly indicate that these zircons did not

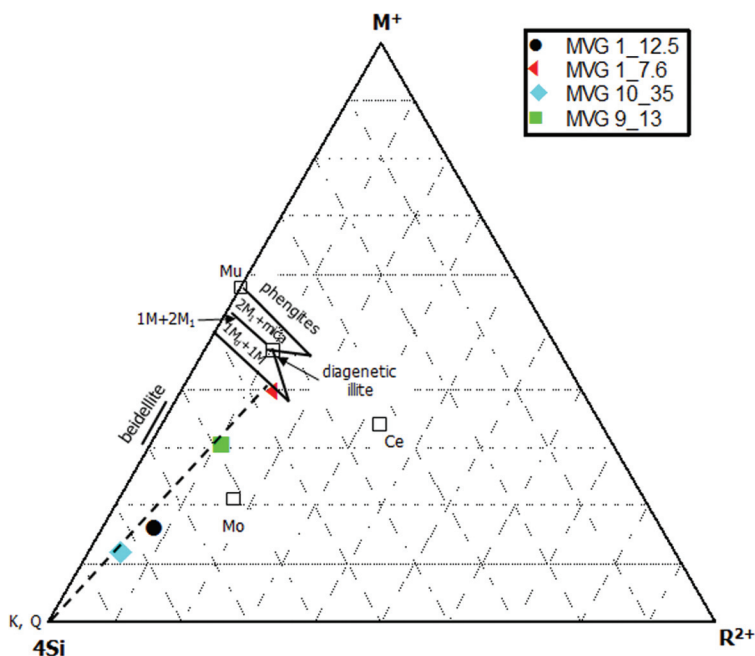


Fig. 10. Projection of the bulk geochemical composition of the M'Vengue K-bentonites from the Francevillian Basin, Gabon on the  $4\text{Si}-\text{M}^+-\text{R}^{2+}$  ternary plot (after Meunier and Velde, 2004). The Francevillian K-bentonites plot along the dashed line with kaolinite and diagenetic illite end-members, which indicates the presence of illite-rich, I/S mixed-layer clay-minerals. The calculated half-unit structural formula of the diagenetic illite is  $(\text{Si}_{3.45}\text{Al}_{0.55})(\text{Al}_{1.71}\text{Fe}_{0.04}\text{Mg}_{0.18}\text{Ti}_{0.03})\text{O}_{10}(\text{OH})_2\text{K}_{0.73}\text{Na}_{0.01}$ . Mu = muscovite; Ce = celadonite; Mo = montmorillonite; K = kaolinite; Q = quartz.

crystallize from the magma, but are older, inherited zircons from either the Archean basement granitoids or older clastic sediments and incorporated into the magma during magmatic activity that produced the Francevillian Basin tephra.

#### Geochemistry and Geochronology

Owing to the susceptibility of the major elements to alteration processes, they cannot be used to investigate the composition of the original magma. However, incompatible trace elements such as Nb, Ta, Ti, Th, Y, Zr, and REEs have been widely used to provide geochemical information on the altered tephra and tectonic setting of the volcanic source (Huff and Turkmenoğlu, 1981; Clayton and others, 1996; Huff and others, 1996; Huff and others, 1998; Christidis and Huff, 2009; Spears, 2012; Huff, 2016; Dai and others, 2017). This is based on the assumption that they are the least affected and least mobile under conditions of low-temperature sedimentary processes (transport, weathering, and diagenesis), low-grade metamorphism, and devitrification of volcanic glass to clay (for example, Winchester and Floyd, 1977; Pearce and others, 1984; Batchelor and Jeppsson, 1994; Huff and others, 1996; Huff and others, 1998; Huff, 2016). The geochemical behavior of these elements depends on the original host phases (volcanic glass or igneous mineral) and the mechanism of alteration. Depletion of Nb and Ta relative to the primitive mantle, moderate enrichments of LILE and LREE, depletion of HFSE and HREE, weak negative Eu anomalies, and low concentrations of REE displayed by the K-bentonites are all characteristic of subduction-related intermediate to felsic calc-alkaline magmas in a continental-arc setting (figs. 11 and 12; Taylor and McLennan, 1985; Huff and others, 1998; Lustrino and Wilson, 2007).

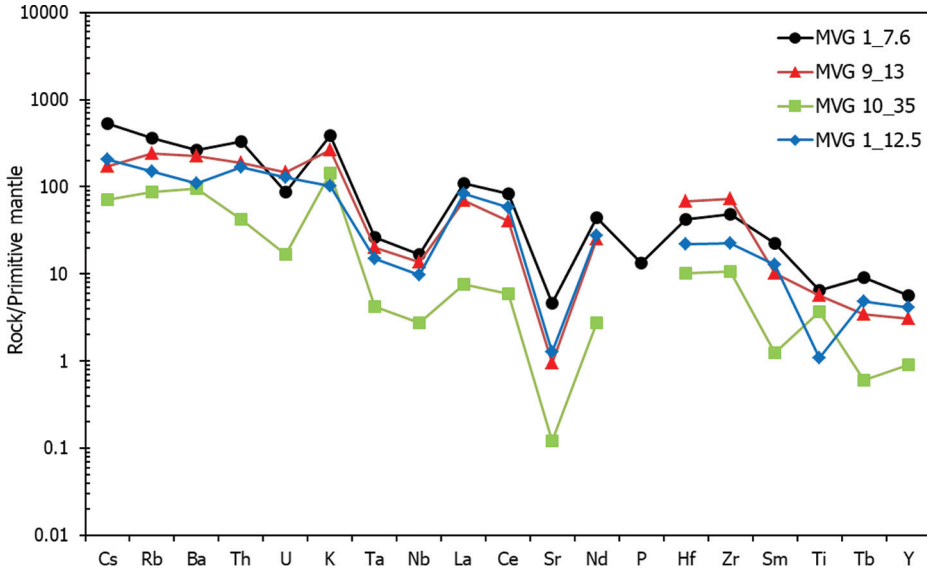


Fig. 11. Primitive mantle-normalized trace-element patterns of the K-bentonites from the Paleoproterozoic Francevillian Basin, Gabon. Phosphorus (P) content in most of the sample is 0. Data for the primitive mantle are from McDonough and Sun, 1995.

Unlike the geochemistry of juvenile, undifferentiated volcanic arcs, enriched LREE, weak negative Eu anomalies, and, in particular, low Th/U ratios of the K-bentonites indicate contribution from a less evolved continental crust (McLennan and others,

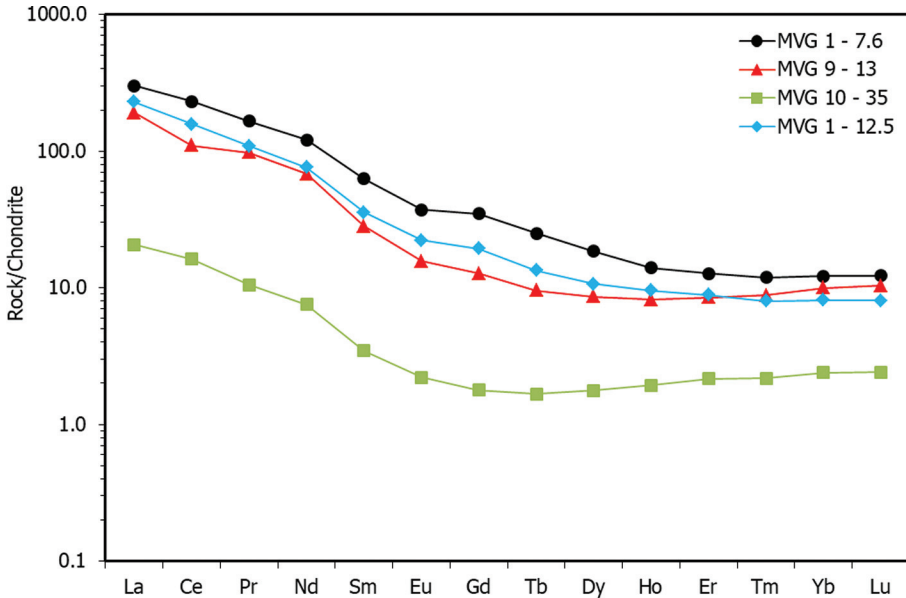


Fig. 12. Chondrite-normalized REE patterns for K-bentonites from the Paleoproterozoic Francevillian Basin, Gabon. Chondrite data are taken from McDonough and Sun (1995).

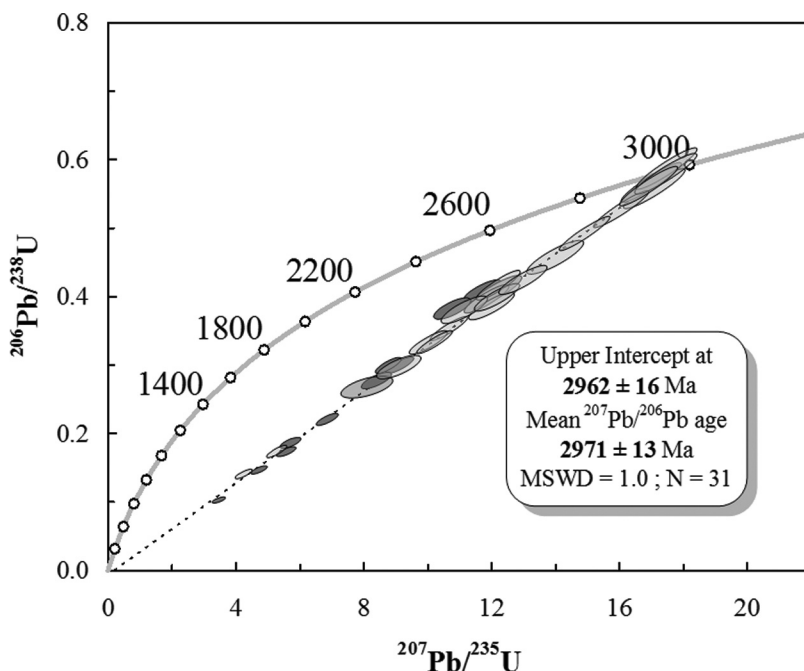


Fig. 13. U-Pb concordia diagram for dated zircons in sample MVG1\_7.6. Computed  $^{207}\text{Pb}/^{206}\text{Pb}$  ages are given with  $2\sigma$  errors. The dark-gray and light-gray shades of ellipses correspond to thin sections prepared parallel and perpendicular to the bedding, respectively. MSWD = mean square of weighted deviates.

1993), favoring intermediate magma composition. Weak negative Eu anomalies could also suggest the following: feldspar was not the main fractionating phase in the melt; oxygen fugacity of the melt was high (Batchelor and Jeppsson, 1994; Huff and others, 1998); incomplete plagioclase crystallization; and intermediate composition of the magma (Huff and others, 1998). In contrast, the pronounced Sr depletion with respect to the primitive mantle, which is shown by all K-bentonite samples, might reflect Sr mobility in fluids during diagenesis (Huff and others, 1998; Kiipli and others, 2010; Huff, 2016).

Discriminant diagrams based on ratios of immobile elements have been applied to provide additional information on the tectonic setting and magma composition of altered volcanic ash. Numerous studies (for example, Huff and Turkmenoğlu, 1981; Clayton and others, 1996; Huff and others, 1996; Huff and others, 1998; Spears, 2012; Dai and others, 2017) applied the  $\text{Zr}/\text{TiO}_2$  vs.  $\text{Nb}/\text{Y}$  plot (originally proposed by Winchester and Floyd, 1977) to assess geochemical fingerprints of the tephra source magma, where  $\text{Zr}/\text{TiO}_2$  ratio is used as an index of magma differentiation and  $\text{Nb}/\text{Y}$  ratio as a measure of alkalinity. However, this discriminant diagram cannot be applied in this study because most of the zircon crystals were inherited and are not representative of the primary magma that produced the tephra. Pearce and others (1984) used immobile trace elements, Nb and Y, to distinguish between within-plate volcanism and that produced in arcs, and Ta and Yb to further separate volcanic-arc granite (VAG) from syn-collisional granites. Orogenic setting for the magmatic system from which the Francevillian Basin K-bentonites were derived can be evaluated using the Nb vs. Y (fig. 14A) and Ta vs. Yb (fig. 14B) diagrams, where the Francevillian Basin K-bentonite plots in the VAG field. These diagrams suggest that magmatism took place in a continental

TABLE 2  
Zircon U-Pb data for the MVG 1\_7.6 K-bentonite obtained by in situ laser ablation MC-ICP-MS

Spot	Pb* (ppm)	Th* (ppm)	U* (ppm)	Th/U	$\frac{^{207}\text{Pb}}{^{235}\text{U}}$	$\frac{^{206}\text{Pb}^2}{^{238}\text{U}}$	$\frac{^{206}\text{Pb}}{^{238}\text{U}}$	$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$	$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$	Rho	$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$	Age (Ma)	$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$	$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$	$\pm 2\sigma$ error
Perpendicular to bedding															
1	128	348	335	1.04	9.074	0.300	0.010	0.219	0.006	0.83	0.219	2976	0.219	0.006	64
2	12	46	34	1.33	8.327	0.278	0.010	0.217	0.007	0.75	0.217	2961	0.217	0.007	77
3	112	147	240	0.61	11.894	0.400	0.012	0.215	0.005	0.89	0.215	2946	0.215	0.005	56
4	64	377	228	1.65	6.794	0.221	0.007	0.223	0.006	0.80	0.223	3004	0.223	0.006	68
5	82	697	351	1.98	5.653	0.187	0.006	0.220	0.007	0.74	0.220	2979	0.220	0.007	78
6	8	47	19	2.42	8.046	0.268	0.013	0.218	0.006	0.59	0.218	2964	0.218	0.006	138
7	42	258	110	2.35	8.707	0.300	0.010	0.210	0.006	0.82	0.210	2909	0.210	0.006	63
8	28	385	122	3.16	5.520	0.174	0.004	0.230	0.007	0.75	0.230	3052	0.230	0.007	75
9	51	1035	385	2.69	3.388	0.166	0.004	0.238	0.008	0.72	0.238	3107	0.238	0.008	81
10	59	528	296	1.78	4.661	0.147	0.005	0.230	0.007	0.76	0.230	3055	0.230	0.007	71
11	38	156	75	2.08	11.671	0.483	0.013	0.207	0.006	0.78	0.207	2883	0.207	0.006	68
12	30	121	64	1.89	10.723	0.383	0.013	0.203	0.006	0.75	0.203	2850	0.203	0.006	73
Parallel to bedding															
13	55	29	85	0.34	17.071	0.788	0.024	0.222	0.005	0.92	0.222	2997	0.222	0.005	69
14	39	21	60	0.34	16.987	0.771	0.024	0.218	0.005	0.93	0.218	2963	0.218	0.005	68
15	47	61	74	0.83	16.036	0.718	0.022	0.221	0.005	0.94	0.221	2985	0.221	0.005	67
16	42	22	62	0.36	17.464	0.791	0.025	0.216	0.005	0.93	0.216	2951	0.216	0.005	68
17	48	83	88	0.94	13.971	0.725	0.020	0.222	0.006	0.85	0.222	2995	0.222	0.006	80
18	33	18	49	0.36	17.441	0.798	0.024	0.219	0.005	0.92	0.219	2970	0.219	0.005	69
19	62	79	109	0.73	14.884	0.657	0.021	0.220	0.005	0.94	0.220	2977	0.220	0.005	66
20	58	31	89	0.35	16.892	0.752	0.023	0.218	0.005	0.94	0.218	2969	0.218	0.005	67
21	40	150	81	1.85	12.153	0.623	0.018	0.216	0.006	0.86	0.216	2950	0.216	0.006	80
22	39	80	84	0.95	11.823	0.575	0.017	0.216	0.005	0.88	0.216	2954	0.216	0.005	75
23	8	84	20	4.19	9.057	0.570	0.014	0.222	0.008	0.75	0.222	2994	0.222	0.008	101
24	34	127	70	1.81	12.172	0.567	0.018	0.212	0.005	0.91	0.212	2922	0.212	0.005	71
25	94	239	200	1.20	10.632	0.486	0.015	0.219	0.005	0.91	0.219	2971	0.219	0.005	70
26	35	170	84	2.02	9.978	0.488	0.014	0.218	0.006	0.86	0.218	2963	0.218	0.006	76
27	133	467	306	2.79	10.182	0.458	0.014	0.222	0.005	0.91	0.222	2994	0.222	0.005	69
28	56	300	108	2.79	11.961	0.591	0.016	0.225	0.006	0.85	0.225	3017	0.225	0.006	77
29	31	210	63	3.31	11.110	0.589	0.016	0.212	0.006	0.82	0.212	2920	0.212	0.006	84
30	82	2129	436	4.88	4.190	0.214	0.006	0.217	0.006	0.83	0.217	2959	0.217	0.006	81
31	79	1497	351	4.26	5.222	0.173	0.007	0.219	0.006	0.85	0.219	2971	0.219	0.006	78
32	88	242	175	1.39	12.129	0.585	0.017	0.221	0.006	0.86	0.221	2987	0.221	0.006	75
33	89	226	167	1.35	12.952	0.620	0.018	0.222	0.006	0.86	0.222	2994	0.222	0.006	75

Note: \* Concentration uncertainty ~20%; † Uncorrected data for non-radiogenic or common Pb; ‡ Error correlation coefficient for  $^{207}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$ .

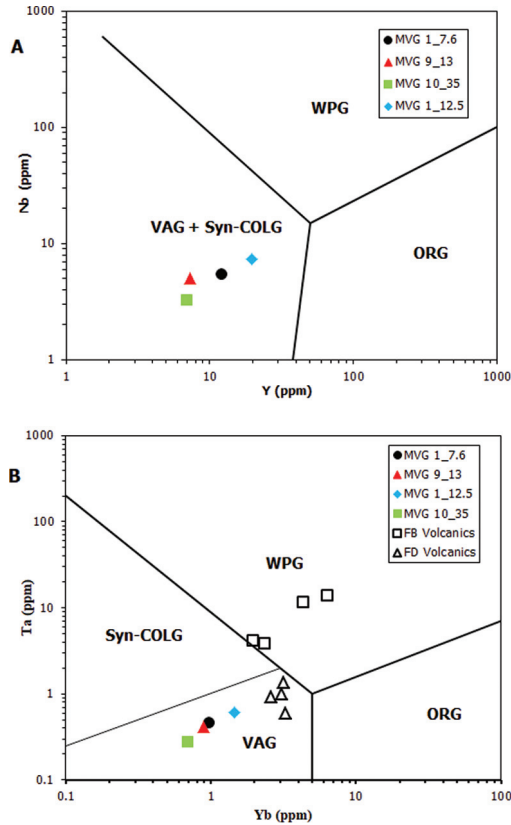


Fig. 14. The Francevillian Basin K-bentonite data plotted on the granite discrimination diagrams of Pearce and others (1984). (A) Nb versus Y; (B) Ta versus Yb. All values were normalized to  $\text{Al}_2\text{O}_3$  ( $[\text{14}/\text{Al}_2\text{O}_3] \times \text{elemental concentration}$ ) to account for residual elemental enrichment during diagenesis (Küplü and others, 2010). Data for volcanics in the FB and FD formations are from Thiéblemont and others (2014). WPG = within-plate granite; ORG = ocean-ridge granite; VAG = volcanic-arc granite; syn-COLG = syn-collisional granite.

arc setting and involved partial melting of the continental crust (Pearce and others, 1984; Huff, 2016).

All the zircons in our samples show the age of the Archean basement. Although this is an unusual case, it is possible that only inherited zircons are present, especially when the magma is of intermediate to felsic composition and similar observations have previously been reported in the literature. For example, Bea and others (2007) documented that most of the zircons in the metavolcanic rocks of Central Iberia are older than the host volcanic rocks. Survival of such inherited zircons was attributed to rapid melt generation, fast magma transfer and cooling at the surface, low magma temperatures to melt zircons, and/or kinetic effects that hindered their melting. Inherited zircons from host rocks or underlying siliciclastic sediments have been documented in multiple studies of felsic volcanic tuffs (Huff and others, 1998; Batchelor and Jeppson, 1999; Spears, 2012; Dai and others, 2017). Pickard (2002, 2003) has shown that both felsic and mafic tuffs associated with the Paleoproterozoic iron formations in the Hamersley Province of Western Australia and Transvaal Basin of South Africa contain inherited zircons re-sedimented from the underlying sedimentary units. We conclude that absence of zircons with Paleoproterozoic ages in the

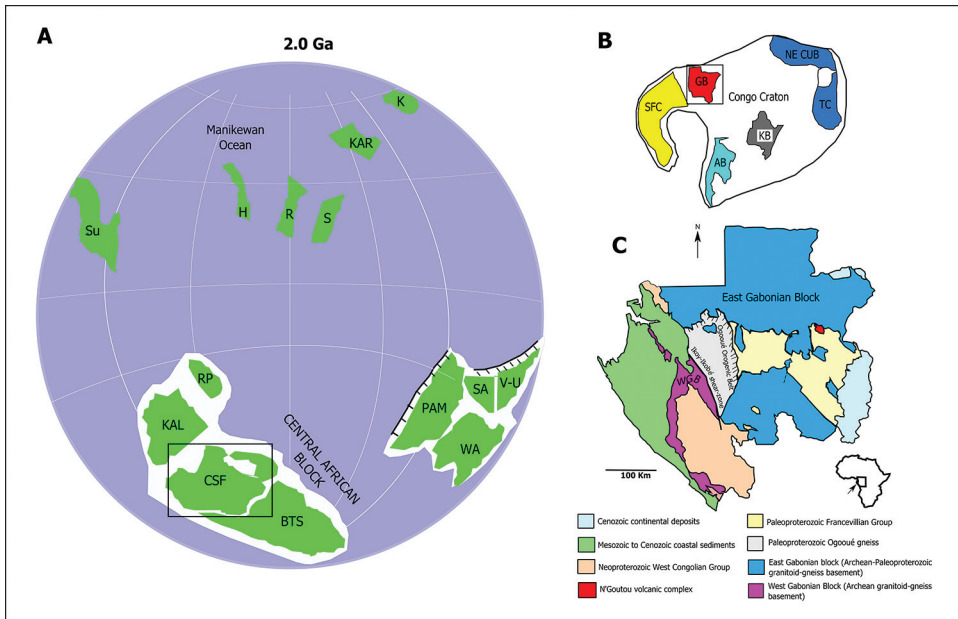


Fig. 15. Paleogeographic reconstructions showing position of the Francevillian Basin within the assembling Nuna (Columbia) supercontinent during the Paleoproterozoic: (A) paleogeographic position of South American and African cratons at ca. 2.0 Ga during the Nuna (Columbia) supercontinent assembly (modified from D'Agrella-Filho and others, 2016; D'Agrella-Filho and Cordani, 2017; abbreviations for the shown cratons: Su = Superior; H = Hearne; R = Rae; S = Slave; KAR = Karelia; K = Kola; RP = Rio de la Plata; KAL = Kalahari; CSF = Congo/São Francisco; BTS = Borborema/Trans-Sahara; PAM = Proto-Amazon; WA = West Africa; SA = Sarmatia; V-U = Volgo-Uralia); (B) The Congo-São Francisco cratons (marked by the rectangle in A and rotated 90° anticlockwise in B) showing the Gabon blocks (marked with the rectangle) and other African blocks within the Congo craton (modified from Fernandez-Alonso and others, 2012; abbreviations: SFC = São Francisco Craton; GB = Gabon Blocks; NE CUB = North-East Congo-Uganda Blocks; TC = Tanzania Craton; KB = Kasal Block; AB = Angola Block); (C) Tectonic map of Gabon showing the West and East Gabonese blocks, the Ogooué Orogenic Belt, N'Goutou Complex, and the Francevillian and other sub-basins where the Francevillian Group is developed (modified from Thiéblemont and others, 2014; WGB = West Gabonian Block).

Francevillian Basin K-bentonites is due to the intermediate magma composition that reflects rapid melt generation, transfer, and cooling in a continental arc setting.

#### *Implications for Evolution of the Francevillian Group*

Earlier studies established that magmatism during deposition of the Francevillian Group resulted in the emplacement of the N'Goutou Complex into the FA and FB formations in the Okondja Basin and deposition of the FD tuffs (Thiéblemont and others, 2014; Weber and others, 2016). These volcanic events were interpreted to record a change from alkaline magmatism of ultramafic and trachytic composition during deposition of the FB Formation to calc-alkaline magmatism of felsic composition during deposition of the FD Formation. The transition from alkaline to calc-alkaline magmatism was linked to a change from a within-plate, rift-related to a subduction-related setting (Thiéblemont and others, 2014; Weber and others, 2016; fig. 14B), leading to a continental collision between the West Congolian and São Francisco cratons that resulted in the Central African Eburnean Orogenic Belt (fig. 15). In Gabon, the East Gabonian block contains the Paleoproterozoic Ogooué fold-and-thrust belt in its western part, while the West Gabonian block hosts 2.08 to 2.04 Ga K-granitoids, emplaced during west-directed subduction of oceanic crust that

separated these blocks (Thiéblemont and others, 2009; Weber and others, 2016). Geochemical similarity of the FB2 member K-bentonites and FD Formation volcanics suggests a similar magmatic source and geodynamic setting despite the difference in their stratigraphic position and mineral composition (fig. 14B; see Thiéblemont and others, 2009). We thus infer that the K-bentonites in the FB Formation were also derived from continental arc volcanoes of the West Gabonian block, implying that the Francevillian Basin developed proximally to the approaching continental arc in a pro-foreland basin typically characterized by a short lifespan and high sedimentation rates (Sinclair and Naylor, 2012). Excellent preservation of lithologies in the Francevillian Basin, recognized both previously (for example, Ossa Ossa and others, 2013; Ngombi-Pemba and others, 2014; Bankole and others, 2015, 2016) and in this study, likely reflects deposition in a distal part of the pro-foreland basin developed in the core of the Nuna (Columbia) supercontinent during the early stage of its assembly (fig. 15).

#### CONCLUSIONS

Sedimentary textures, mineralogy, and chemical composition demonstrate the bentonite nature of the olive-green to light-red thin beds in the *ca.* 2.1 Ga Francevillian Basin, Gabon. Their clay mineral composition suggests a diagenetic origin via smectite to illite transformation over a prolonged period of time at low temperature. The chemical composition of the FB2 member K-bentonite beds suggests derivation from intermediate to felsic magma with a calc-alkaline affinity similar to that of the stratigraphically higher FD Formation volcanics and is consistent with proximity to the continental arc developed on the West Gabonian block. We infer that the Francevillian Basin was developed in a pro-foreland setting characterized by a short lifespan and high sedimentation rates. The zircon shapes and U-Pb zircon dates from the K-bentonite suggest inheritance from the Archean basement during magmatic activity. These K-bentonites are the oldest bentonites that have been so far reported and their deposition as well as preservation likely reflects initiation of the Nuna (Columbia) supercontinent assembly that subsequently locked this basin in the core of the supercontinent (fig. 15). These K-bentonites could thus serve as a potential stratigraphic correlation marker for the Gabonian and adjacent cratons at *ca.* 2.1 Ga.

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APPENDIX

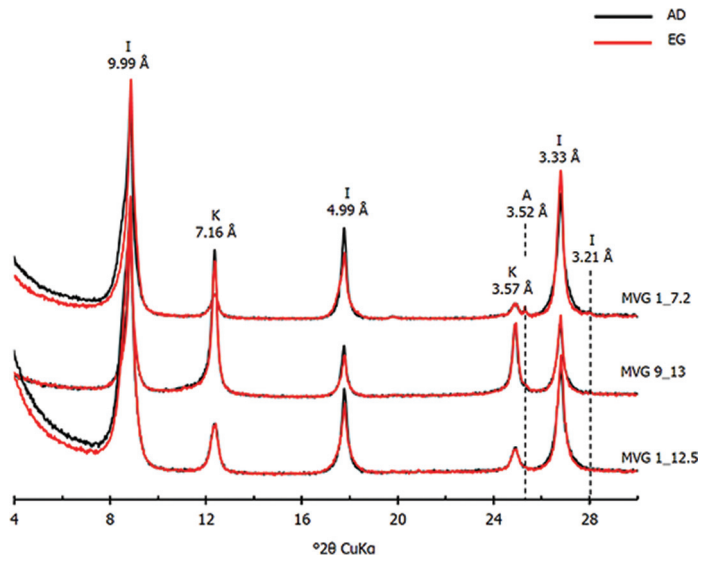


Fig. A-1. X-ray diffraction (XRD) patterns of oriented  $<2 \mu\text{m}$  clay fraction in air-dried (AD) and ethylene glycol-saturated (EG) preparations of the Paleoproterozoic Francevillian Basin K-bentonites.

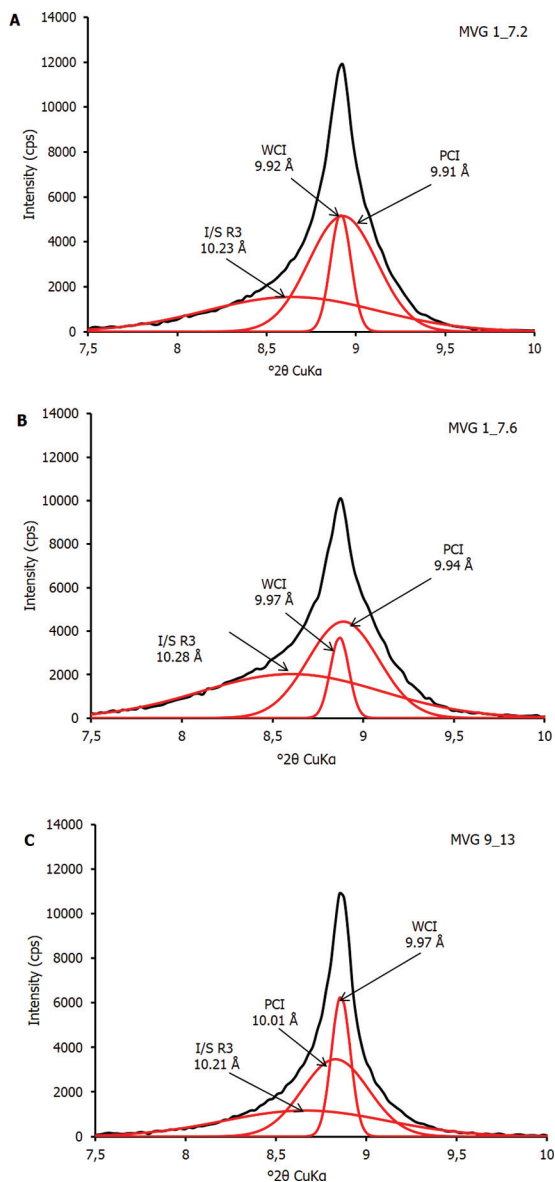


Fig. A-2. Decomposed 001 illite peaks of  $<2 \mu\text{m}$  clay fraction in ethylene-glycol (EG) preparations of the Paleoproterozoic Francevillian Basin K-bentonites: (A) MVG 1\_7.2; (B) MVG 1\_7.6; and (C) MVG 9\_13. WCI peaks are narrow, while the PCI and I/S peaks are broad (WCI = well crystallized illite; PCI = poorly crystallized illite; I/S = illite-smectite mixed layer clay minerals).

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