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Geological, mineralogical and chemical characterization of Devonian kaolinite-bearing sediments for further applications in the ceramic (tiles) industry in La Paz, Bolivia

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Abstract Clay minerals are widely distributed in Bolivia; among them, illitic clays are most common in the Altiplano where they are mined for use in the ceramic industry that has been growing in the last few years. In addition to illitic sediments, kaolinitic sediments have been recently discovered in sedimentary units in the Bolivian Altiplano. Residual ball clay occurrences in Devonian sedimentary units were studied as part of this work. Geological mapping and geophysical studies (ERT and GPR) were done for better understanding the origin of the deposits and were part of a preliminary study of the mineral potential to define the relationship with the host rock. Chemical and mineralogical techniques such as X-Ray Diffraction, Scanning Electron Microscopy and Inductively Coupled Plasma analyses were performed in samples from the studied area to verify the presence of kaolinite. Atterberg limits and behaviour of the raw material in ceramic specimens supported by chemical analyses show that this material is suitable for manufacturing tile ceramics. This study provides fundamental knowledge for deposit exploitation and future generation of an alternative source of employment for the inhabitants of Micaya.

Keywords Kaolinite · Ball clays · Altiplano · Ceramics · Siltstones

Introduction

Kaolinitic sedimentary clays are referred as “Ball clays”; and are amended to ceramic bodies. Kaolinitic clays are used in ceramic manufacture to add plasticity and strength to the ceramic body (McCuistion and Wilson 2006). They are generally composed of clay-size particles of kaolinite, illite, sericite and poorly crystallized fine-grained quartz (Mooney 1996; McCuistion and Wilson 2006). The term ceramic “body” is used to describe the starting material composed mainly of clay, to be used for a specific ceramic purpose.

The chemical composition of kaolinite is $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, having 39.8 wt% alumina, 46.3 wt% silica and 13.9 wt% water. It is an important industrial mineral for several applications including paper coating and filling, ceramics, paints and plastics (Murray and Keller 1993). A common assemblage of Ball clay deposits includes kaolinite, quartz and minor amounts of halloysite, muscovite and feldspars (Murray 1988). Kaolinite is mainly processed as a raw material for use in the ceramic industry; for manufacture of wall tiles, white wares, chemical, and scientific wares, sanitary wares and refractories. Depending on the kaolinite content in ball clays, some deposits are suitable as fillers in paper coating and paints (Murray and Keller 1993).

Geologic occurrences of kaolinite

Kaolinite-bearing deposits can occur in primary residual and secondary diagenetic environments (Murray and Keller 1993). Keller (1982) describes three geologic environments where kaolinite forms. The first occurs in low temperature weathering environments, the second takes place in

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hydrothermal systems and the third forms from the crystallization process from colloid-size sediment whose chemical composition is congruent with that of kaolinite. Kaolinite can form at relatively low temperature and pressure from alteration of primary potassium-bearing minerals where the most common parent minerals are feldspar and muscovite (Murray 1988). An example of a low temperature kaolinite deposits is in Santa Cruz, Bolivia, where low temperature alteration of pegmatites have formed economic kaolinite deposits. Although the most common kaolinite deposits were formed by alteration of granitic rocks, some deposits have been formed from arkosic sediments that were altered primarily by groundwater after deposition (Murray 1988; Murray and Keller 1993).

Grahamstown, South Africa is one of the best studied kaolinite deposits hosted in sedimentary rocks (Murray and Smith 1973; Murray 1988; Jacob et al. 2004; Agnello 2005).

The ultimate industrial use of kaolinite is determined by the geological conditions in which a kaolinitic deposit was formed and the physical and chemical properties of the associated mineral assemblage (Keller 1982; Murray and Keller 1993). Knowledge of the origin, diagenesis and chemical composition of the clay is essential for the exploitation and use of the raw material for ceramic production (Sanfeliu and Jordan 2009).

Major kaolin producing countries are the United States (5480 Mt), Brazil (2050 Mt) and Czech Republic (3550 Mt) (Virta 2012). Three main ball clay deposits have been identified in Bolivia, which are located in Batallas, Karhuisa and Warmimarka (Fig. 1), where illite is the plastic mineralogical phase identified in these deposits (Escobar et al. 1999). Illite and kaolinite occurs in sediments and rocks in the Bolivian deposits and the material is currently mined for use in the construction industry (Escobar et al. 1999). Although these deposits are actively mined, they are poorly characterized.

The study area is located in Micaya, La Paz, where kaolinite bearing sediments were hand mined by the local inhabitants for handmade kitchen pots. The kaolinitic sediments in the Micaya area were first studied by Blanco et al. (2005); their physical properties including texture were described by Zeballos et al. (2009), who identified quartz, muscovite and feldspar as important constituents of the kaolinite occurrences. The physical properties including textural characteristics such as grain size are relevant to the material suitability for use in ceramics. Complementary geological, mineralogical, chemical and physical characterization tests were performed in selected rock samples to define the origin of the deposits in the Micaya area and its suitability for use in ceramics manufacture. Geophysical studies were used to also help to identify the spatial relationship of the kaolinite-bearing layers.

There are few studies concerning mineralogical characterization and formation of kaolinite bearing sediments in the Bolivian territory. Previous studies identify kaolin as a by-product of intense alteration of pegmatites such as in Santa Cruz and as a by-product of intense alteration of granitic rocks such as in La Paz and Oruro (Orris et al. 1992; Escobar et al. 1999). However, the kaolinitic materials described in sedimentary units in the Altiplano, are scarcely mentioned and barely studied, hence the importance of the current work.

Geological setting

Regional geologic framework

The sedimentary sequence in the Altiplano is represented by Silurian and Devonian units, composed of sandstones grading into pelitic rocks in normal graded sequences (GEOBOL 1995), overlain by limestones from the Cumana unit, and matrix supported conglomerates and tuffs intercalated with Neogene siltstones.

Porphyritic rocks from the Letanias and Comanche–Miriquire complex intrude the Palaeozoic sequence (Redwood 1986). The Letanias complex is calcalkaline and dacitic to andesitic in composition (Redwood 1986). Accessory minerals such as sphene, zircon and apatite were reported. All volcanic rocks display a holocrystalline matrix and flow texture. These rocks have been dated by K–Ar method at 16.6 ± 0.40 Ma (Redwood 1986). The Comanche–Miriquire porphyritic complex is composed of dacites, rhyolites and andesites and has been dated at 15.7–17.9 Ma by K–Ar (Redwood 1986).

Cenozoic intrusive and volcanic rocks in the study area resulted in the deposition of pyroclastic materials formed during Neogene volcanism. The deposition of fine grained pyroclastic material filled paleo valleys and modified the relief of the area (Soria 1980). Ages of preserved tuffs in the Remedios Formation range from 5.2 to 4.6 Ma (GEOBOL 1995).

Local geology

The local stratigraphy of Micaya (Fig. 2) consists of Palaeozoic and Cenozoic sedimentary rocks. The Palaeozoic sedimentary rocks are intruded by Cenozoic, dacitic and andesitic rocks. Tertiary pyroclastic rocks including ash-flow tuffs are exposed in the area. The lithostratigraphic succession is given in Fig. 3. Vila Vila and Sica Sica formations are the host units for the studied clay materials (Fig. 3). The terrain is characterized by wide fluvial valleys with adjacent upland areas including the Asunkollu (4188 m) and Nunu Kkollu hills (4200 m) (Fig. 2).

Fig. 1 Location map of the study area, Micaya and location of Batallas, Karhuisa and Warmimarka illitic deposits studied by Escobar et al. (1999)

Structural geology

The main structures in the Micaya area have a NW–SE (Fig. 2) orientation and they formed in response to the Andean orogeny, which is characterized by (SW–NE) directed compressional events. The deformation caused by the Andean uplift overprints earlier compressive deformation ascribed to the Hercynian orogeny (Martinez and Vargas 1990).

Faults in the Vila Vila and Sica Sica units are particularly important, because they form permeable hydrologic flow-paths, resulting in highly weathered siltstones, which are the parental sediments of the kaolinitic material. Enhanced weathering of siltstones along the fault zones

due to water–rock interaction is thought to be an important process in forming secondary kaolinite (Zeballos et al. 2009).

Cenozoic volcanism

Cenozoic magmatism resulted in the deposition of fine pyroclastic materials (Remedios Formation) and intrusion of dacitic and andesitic subvolcanic rocks of the Letanias Complex (Soria 1980). Sedimentary units in the area were locally deformed causing visible folds and faults. The calc-alkaline porphyritic rocks of the Letanias Complex (16.6 ± 0.40 Ma by K–Ar; Redwood 1986) contain an abundance of sanidine phenocrysts, minor plagioclase and

Fig. 2 Geologic map of Micaya modified from the Calamarca geologic map printed by GEOBOL (1995)

biotite. Some igneous bodies also contain rounded quartz phenocrysts and green or brown hornblende, with accessory sphene, zircon and apatite.

Materials and methods

Geological mapping (Figs. 2, 3) and structural profiles (Fig. 4a, b) were prepared to interpret the kaolinite-bearing deposit of Micaya in a geological context. Twenty semi-consolidated representative samples, 2–3 kg each were collected. Ten semiconsolidated clay samples from the Vila Vila formation and ten samples from the Sica Sica formation were also collected for analyses.

Chemical analyses were performed using Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP–AES) on the most representative samples and were carried out by ALS Scandinavia. Prior to the analysis the samples were dried at 105 °C, using a 0.1 g sample digested with

0.375 g LiBO_2 and dissolved in HNO_3 . Loss on ignition (LOI) was determined gravimetrically by heating powders to 1000 °C for 1 h. ICP–AES analyses were completed on representative samples and the results are reported in “Appendix Table 1”. Detection limits for major elements are 0.01 wt% and detection limits for most trace elements are 1–10 ppb. Mineralogy was determined by X-ray powder diffraction (Fig. 5) by a X’Pert3 PANalytical instrument using $\text{Cu K}\alpha$ radiation and time step increments of 0.010°/s. Mineral identification and quantification were determined with the help of the X’pert High Score Plus software. The quantification results were performed according to the Rietveld method (Rietveld 1969). The mineral kaolinite has a characteristic X-ray spectral peak at 12.32° (7.1 Å) (Brown and Brindley 1980; Moore and Reynolds 1997).

The microstructure of selected samples was investigated by scanning electron microscopy (Fig. 6a, b) (SEM, Magellan UHR) and Energy Dispersive X-ray Spectroscopy

GENERALIZED STRATIGRAPHIC COLUMN

Fig. 3 Regional stratigraphic column of Micaya area and local stratigraphic columns based in geophysical tests

(EDX, X-MAX 80 mm², Oxford Instruments), in freshly broken surfaces of clays. An accelerating voltage of 1 kV and a current of 6.3 pA was used for high resolution imaging. Microanalyses were performed on samples mounted on an aluminium stub after powder samples were dispersed and dried in chloroform.

Preliminary physical tests commonly used on ceramic body were performed on ten ceramic specimens. Five samples from each deposit were selected and tested for: plasticity (ASTM D4318 2010), shrinkage (ASTM C326-09 2009), water absorption (ASTM C373-14 2014), Mohs scale hardness, bending strength (IBNORCA 2014; NB/ISO 10545-4:2005 2014) ("Appendix Table 2") and fired color (Munsell Chart 2009). The samples were dried and wet-ground (jaw crusher and porcelain grinder for 4 h; 350

mesh). Resulting powders were mixed, humidified (moisture content 8.25 wt%) and then pressed into bars (18 MPa; size 8.025 × 29.5 × 6.20 ± 1.0 mm; clay content 100 wt%). After drying (48 h at room temperature) the bars were fired (8 h; maximum temperature 1250 °C). The ceramic specimens were characterized by measuring the size variations after 24 and 48 h of pressing.

Geoelectric and electromagnetic geophysical tests

Geophysical tests (Figs. 7, 8) were performed using Electrical resistivity tomography (ERT) and Georadar (GPR). Both methods were used for a basic estimation of the spatial relationship of the kaolinitic layers within the host rocks. Five lines were established using georesistivity

Fig. 4 **a** Geological profile (A–B) of the SW deposit and **b** geological profile (C–D) of the NE studied deposit. From the geologic sheet of Micaya

Fig. 5 Comparative XRD pattern of the kaolinitic layers. Four minerals were identified: Quartz (3.366 Å), muscovite (9.908 Å), kaolinite (7.122 Å) and feldspar (3.239 Å)

equipment. The resistivity instrument used was a OYO Model geo-receptor JP-600 brand. It has a sensitivity of 0.01 mV and digital recording capability. The unit operates at 2.5 amps and has a variable voltage of up to 1000 V. It operates using a 12 V battery and has four cable spools

(100 m each) and 30 copper electrodes with a linear array of 10 m. The GPR studies were carried out in seven lines using a GEORADAR ZOND-12E instrument equipped with a 75 MHz monostatic antenna applying time windows of 120 ns, with 40 scans/s, and 512 samples per scan.

Fig. 6 SEM backscattered images of **a** Muscovite stacks in the NE deposit (Sica Sica sedimentary unit) and **b** microphotograph of the kaolinitic plates for the SW deposit (Vila Vila sedimentary unit) exhibit irregular edges, a characteristic texture in kaolinites form sedimentary rocks. Mineral abbreviations according to Kretz (1983)

Electrical and electromagnetic methods can be used to map subsurface variability according to electrical properties, caused by changes in lithology, structure and alteration. The geoelectric method (ERT) is used to measure the apparent resistivity (conductivity) of the rocks (János 2009). This method is based on the application of electric current into analysed bedrock and measurement of the intensity to its conductance. In electromagnetic methods (GPR), the electric current in the rocks induces a magnetic field (János 2009). The depth of investigation can range from less than a meter in the case of ground penetrating radar depending on the antenna used in the test (900 MHz—1.5 m depth; 200 MHz—9 m depth; 80–16 MHz—

10–30 m depth), to tens and hundreds of meters depth for most other methods. Resolution of targets and detectability tend to decrease with increasing depth of burial (Watson et al. 2001).

Analytical results

Chemistry, mineralogy and microstructure

The chemistry and qualitative mineral assemblage of selected samples from Vila Vila (SW in the study area) and Sica Sica layers (NE in the study area) are shown in Appendix Table 1 and Fig. 5. The mineral assemblage of each layer was determined by XRD analyses showing a dominance of quartz, muscovite, kaolinite with subordinate feldspar, in the SW deposit; and quartz, muscovite and kaolinite in the NE deposit.

Silica content is consistently higher in Vila Vila samples (70.5–74 wt%) compared to the Sica Sica material (63.2–67.1 wt%). The Al_2O_3 content is higher in Sica Sica sediments (20.9–23.8 wt%) compared to Vila Vila sediments (17.0–17.9 wt%). The potassium content is similar in both layers and resides in muscovite and feldspars. The chemical results are consistent with the mineralogy of the material containing quartz, muscovite, kaolinite and lesser amounts of feldspars as shown in the XRD pattern (3.239 Å) (Fig. 5). The iron content ranges from 1.27 to 1.87 wt%. According to the Munsell color chart classification (2009), the raw ball clays are white (N9) to medium light grey color (N6) after kiln firing, which is consistent with the low iron content.

Mineralogical (Figs. 5, 6) and geochemical studies (“Appendix Table 1”) have been performed in both kaolinitic beds from Micaya. Four mineralogical phases have been identified in the SW deposit (Vila Vila unit) (Fig. 5): quartz 56.3 wt%, muscovite 12.2 wt%, kaolinite 24.9 wt%, and feldspar 6.7 wt%. The studied material from the Sica Sica unit (NE deposit) was composed of quartz 50.8 wt%, muscovite 35.4 wt%, and kaolinite 13.8 wt% (Fig. 5).

The major element chemical composition of the Vila Vila unit is: SiO_2 (70.5–74.2 wt%) and Al_2O_3 (17–17.9 wt%), followed by 3.8–4 wt% of K_2O and comprising >90 % wt% total (on a volatile free basis) (“Appendix Table 1”). The Sica Sica layer compared to the Vila Vila unit is lower in SiO_2 (63.2–67.1 wt%), has higher Al_2O_3 (20.9–23.8 wt%) content and has a similar of K_2O (3–4.9 wt%) composition, comprising >95 % wt% (on a volatile free basis) (“Appendix Table 2”).

The microstructure of the samples is shown in Fig. 6a and b. The SW deposit is composed mainly of kaolinite plates; the NE deposit mainly contains muscovite stacks. Secondary kaolinite after muscovite is observed in

Fig. 7 Geoelectric tomography and ground penetrating radar results of the SW deposit

muscovite rich siltstones. The siltstones also contain quartz. Kaolinite is observed in both the SW and NE materials. The result of the Atterberg limits test shows a plasticity index of 4.03 for the SW samples and 4.01 for the NE samples, both reflecting zero plasticity according to the Casagrande chart (Casagrande 1932). These results reflect silt with low plasticity. The low plasticity is consistent with the predominant clay mineral being kaolinite (Bain 1971). “Appendix Table 2” shows the result of the physical tests performed on the ceramic specimens. The above results suggest that the kaolinite bearing materials are a suitable source for ceramic body.

Geophysical test

According to János (2009), the resistivity method has been proven to be useful in determining thickness and extent of horizontally stratified clay, sand and gravel deposits, being an important tool in geological, environmental and

engineering surveys (Busby et al. 2004; de Oliveira Braga et al. 2006; Pánek et al. 2006; El Assel et al. 2011; Kumar 2012). Geoelectrical and electromagnetics methods are thought to be reliable and low cost methods to investigate underground lithology and subsurface structures and are easy to handle during field work (Burley et al. 1978; Sanner and Abbas 1998; Watson et al. 2001; EL-Qady et al. 2005).

Geophysical studies in the Micaya area (Fig. 2) were carried out through five resistivity lines (150 m) and seven GEORADAR lines. GEORADAR was performed in both occurrences to identify the spatial relationship of the kaolinite-bearing layers. The electrical resistivity tomography results are consistent with the ground penetrating radar results; both geophysical techniques show three lithological layers for the SW deposits: sandstones, conglomerates and clays (Fig. 7), and sandstones, siltstones and clays for the N–E occurrence (Fig. 8). Geographical position line length and approximate thickness of lithologic units are given in “Appendix Tables 4 and 5”.

Fig. 8 Geoelectric tomography and ground penetrating radar results of the NE deposit

Fig. 9 Kaolinitic occurrence located in Micaya

Discussion and conclusions

Geological mapping (Fig. 2) in Micaya (La Paz) has identified two kaolinite-bearing occurrences in Devonian units consisting of sandstones in the Vila Vila formation and sandstones and siltstones in the Sica Sica Formation (Fig. 3). Kaolinitic material in the study area has been historically mined and minor mining is ongoing in the area (Fig. 9). The mined material has been used locally to manufacture white handmade kitchenware such as pots and dishes. Kaolinite is thought to be formed by enhanced weathering of siltstones containing potassium-

rich minerals, such as muscovite and feldspars. Diagenetic kaolinite formation was aided by groundwater that interacted with rocks along permeable zones in folds and faults which increases the speed of breakdown of the primary minerals to clay minerals.

Mineralogical and geochemical studies performed in the kaolinitic beds show similarities in both materials. Although quartz, muscovite and kaolinite are the main mineralogical phases in both deposits, feldspar (6.7 wt%) is only observed in the Vila Vila unit (Fig. 5), the color and the fine-grained size and texture of the materials are similar.

The SiO_2 is consistently higher in the Vila Vila samples compared to the Sica Sica material ("Appendix Table 1"). A higher SiO_2 content is a desirable quality for floor tile ceramic materials. The Al_2O_3 content is higher in the Sica Sica sediments due the amount of muscovite. The K_2O content is similar in both layers and hosted in minerals such as feldspars and muscovite in the Vila Vila sediments and muscovite in the Sica Sica sediments. Both compositions indicate a favourable composition for ceramic materials production in which kaolinite will give plasticity to the mixture, whereas quartz and feldspar will increase the strength (McCuistion and Wilson 2006; Mooney 1996). The iron concentration is low (<2 wt%) for both layers ("Appendix Table 1"), and is desirable for tile manufacture.

Although "Ball clays" are well known for high plasticity and according to Bain (1971), kaolinitic materials derived from weathered sedimentary rocks tend to have a

high plasticity index (>10). This property can be reduced by the semiconsolidated character of the material or grain size of the material. In the Micaya samples, the reduction in the plasticity index of <5 is due to poor induration of the deposit. The plasticity index could affect, whether it can be used in ceramic body for various applications. Nonetheless ball clays will increase the green (unfired) strength after pressing (Mooney 1996; McCuistion and Wilson 2006). The green strength quality is visible in Appendix Table 2, where the ceramic specimens display high bending strength of $>55 \text{ N/mm}^2$. The desirable average range in ceramic tiles must reach at least $50\text{--}55 \text{ N/mm}^2$ (ISO 10545-4).

Both deposits show similar chemical and mineralogical characteristics, suggesting in situ formation as a result of a contemporaneous alteration event affecting siltstones in both sedimentary units. Scanning electron microscopy analyses shows kaolinite pseudomorphs after muscovite in both areas (Fig. 6a), indicating diagenetic transformation of muscovite to kaolinite. These muscovite stacks contain voids within the plates due to the release of potassium during kaolinitization (Stoch and Sikora 1976; Manju et al. 2001). The rock-forming mineral assemblage also suggests muscovite as the parent mineral for the kaolinite crystallization as no other phase has been identified as a likely precursor to kaolinite. Based on the shape of the kaolinite plates visible in the SEM images (Fig. 6b) and the kaolinite peaks from the XRD pattern (Fig. 5), we could conclude that the studied material exhibits poor crystallinity. The composition, heterogeneity and the irregular angular edges (Keller 1985; Fig. 6a, b) suggest primary formation, which is characteristic of actively growing crystals as a result of the on-going weathering process and is an indication of in situ formation. Differences in the kaolinite crystallization could be due to the physical characteristics of the host rock. Sandstones are competent and sometimes brittle during deformation resulting in a highly fractured rock with a high hydraulic conductivity compared with more plastic materials. Mineralogical and chemical similarities of both studied materials are apparent as the characterization reflects; therefore the samples also show similarities in the results of the physical tests for ceramic applications (Appendix Table 2).

Kaolinite bearing sediments were identified through geological mapping (Figs. 9, 10) and aided by mineralogical and physical tests. The geophysical results provide insight for a better understanding of the spatial relationship of the kaolinite-bearing units and the material potential for future exploitation.

The Micaya area is relatively arid; therefore the degree of water saturation in the soil is minor. Nevertheless the morphology of the area contributes to minor water accumulations during the rainy season. The reflections observed in geophysical profiles are mainly caused by the

Fig. 10 Mine workings present in the area

differences in lithology among the materials in contact, caused by the facies change within stratigraphic units. The ERT method does not provide a unique interpretation and is also insensitive to surface layers or features having similar electrical properties such as clays and siltstones and the GPR has limited depth of penetration in clay sediments. The frequency used must be high enough to resolve the target size and geometry, as the frequency increases small-scale features such as fine scale bedding, cracks and joints that become radar targets which reflect and scatter the signal. This results in clutter within the recorded data and reduces the amount of energy penetrating to depth. In addition, as the radar frequency increases the signal attenuation within the ground increases (Busby et al. 2004). Nevertheless, the combination of ERT and GPR methods has been able to distinguish two sedimentary units in the SW deposit (Fig. 7) having distinct geophysical signature, with a good correlation between them and one sedimentary unit in the NE deposit (Fig. 8). In each deposit three lithologic units were identified:

In the SW deposit: *Lithologic unit 1*, is associated with Devonian sandstones and clays from the Vila Vila Formation (Fig. 3) and conglomerates from the Umala Formation (Fig. 3). It has a regular surface morphology according to the local erosion level. This layer has a high

GPR signature; mainly due to the fractured character of the strata. The material has been identified as fractured sandstones. In general, the ERT profiles show resistivities between 30 and 6000 Ω m for this level. *Lithologic unit 2*, is correlated to the first stratigraphic series that corresponds to irregular interbedded thin clay layers. The GPR-38 MHz profiles show some good reflectors that coincide with the interpretation of the geological mapping, although the lithologic contact between the upper and lower units is not well defined due the signature attenuation caused by the clays. The electric response for this layer is located below 80 Ω m. *Lithologic unit 3*, is thicker than the overlying units (about 50 m; “Appendix Table 3”) and is related to the stratigraphic series consisting of a continuous sandstone beds. The electric response is over 1900 Ω m.

In the NE deposit: *Lithologic unit 1* is the uppermost unit and is associated with Devonian sandstones and siltstones of the Sica Sica Formation (Fig. 3). This layer presents a high GPR signature mainly due the fractured character of the sandstone. In general, the ERT profiles show resistivities between 20 and 750 Ω m for this level. *Lithologic unit 2* is the second identified unit and corresponds to an irregular interbedded thin clay layer. The lithologic contacts between the upper and lower units are not well defined. The electric response for this layer is located below 300 Ω m. *Lithologic unit 3* is thicker than the previous units (about 30 m; “Appendix Table 3”) and is related to a continuous sandstone horizon. In this case the electric response is over 9000 Ω m.

The geophysical methods used in the Micaya area for a preliminary investigation of the spatial relationship of the kaolinite-bearing layers have been proven effective in characterizing the mineralogical occurrences. Both, the GPR and ERT methods show similar results. The ERT method proved to be more effective in determining clay layer thickness in both occurrences, although the resolution has been reduced due to the electrode linear array configuration. According to Watson et al. (2001) and Busby et al. (2004) the GPR method is not recommended for clayey or very conductive terrains due to the attenuation of the radar signal by the conductive ground, so it is not possible to observe well defined lithologic contacts between clay and non-clay layers.

The results of the geological, analytical and geophysical investigations performed in the Micaya area provide important information concerning the economic potential of the sediments as an exploitable source of kaolinite. The important features of the resources are:

- Important potential for local use in ceramics manufacture. The deposit meets local standards for use in ceramic body.

- The mineral mixtures are fine grained which reduces energy use required for grinding. The mineral association is simple (quartz–kaolinite–muscovite–feldspar) and the presence of SiO_2 , Al_2O_3 and Fe_2O_3 are within the allowable international determined parameters for white ceramic formulations, according to international and national parameters.
- The study area is accessible using existing infrastructure.

An assessment of pelitic sediments for use in ceramics includes the following characteristics: (1) reliable quantity of quartz, and clay; (2) low iron content and (3) good quality of the final products. Chemical composition of materials that can be unfavourable for use in ceramics are high SiO_2 and Fe_2O_3 concentrations, this composition raise the melting point of the mixture and adversely affects the quality of a raw material. On the other hand, lower quartz content reduces the strength of the ceramic specimen, also affecting the quality of the end product. High Fe_2O_3 concentrations are tolerable for building materials such as bricks. High Fe_2O_3 content however would prevent use for ceramic manufacture, because light colors are required. All these required characteristics are intimately related to the origin of the raw material.

The sedimentary source of the kaolinite-bearing sediments in Micaya is similar to those pelitic sediments studied in the Grahamstown deposits in South Africa. The pelitic sediments from Grahamstown are currently used in the ceramic industry and are acceptable for use in the ceramic production of wall tiles and white wares (Agnello 2005).

The XRD pattern (Fig. 5) of the studied mixtures supported by whole rock chemical analyses (“Appendix Table 1”) defines the mineralogical composition of the kaolinitic materials as quartz and kaolinite along with muscovite and minor amounts of feldspar in each sedimentary unit. Based on the shape of the kaolinite plates and the kaolinite peaks from XRD pattern we infer that the studied material exhibits poor crystallization and the heterogeneity of the composition and the irregular edges suggest primary formation. Therefore we conclude that the kaolinite-bearing sediments located in Micaya are good raw materials for the ceramic tile industry; they are easy to access and easy to process due to the mineralogy of the material and feasibility for local mining and production.

Appendix 1

See Tables 1 and 2.

Table 1 Chemical analyses of the Vila Vila kaolinite bearing sediments

Location	Samples									
	M-1	M-2	M-3	M-4	M-5	M-6	M-7	M-8	M-9	M-10
Vila Vila										
SiO ₂	71.30	72.70	74.20	72.30	72.10	71.40	71.50	72.00	70.50	72.40
Al ₂ O ₃	17.30	17.60	17.90	17.60	17.60	17.40	17.30	17.50	17.00	17.50
CaO	0.14	0.14	0.14	0.15	0.14	0.14	0.14	0.14	0.13	0.14
Fe ₂ O ₃	1.28	1.29	1.32	1.30	1.29	1.30	1.29	1.32	1.27	1.31
K ₂ O	3.83	3.87	3.96	4.01	3.90	3.85	3.88	3.92	3.82	3.93
MgO	0.68	0.69	0.70	0.69	0.69	0.69	0.69	0.70	0.67	0.69
MnO	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Na ₂ O	0.10	0.10	0.10	0.11	0.10	0.10	0.10	0.11	0.10	0.10
P ₂ O ₅	0.07	0.07	0.08	0.07	0.08	0.07	0.07	0.08	0.07	0.08
TiO ₂	0.96	0.97	0.99	0.98	0.97	0.96	0.95	0.97	0.94	0.97
LOI	4.40	4.40	4.30	4.30	4.40	4.40	4.40	4.40	4.30	4.40
Total	100.09	101.85	103.71	101.53	101.29	100.33	100.34	101.16	98.84	101.54

Table 2 Chemical analyses of the Sica Sica kaolinite bearing sediments

Location	Samples									
Sica Sica	M-1	M-2	M-3	M-4	M-5	M-6	M-7	M-8	M-9	M-10
SiO ₂	65.20	67.10	65.30	63.20	65.90	66.20	66.90	65.40	66.30	65.70
Al ₂ O ₃	21.80	20.90	22.90	23.80	22.30	21.90	22.80	21.90	22.80	21.90
CaO	0.47	0.48	0.47	0.47	0.48	0.47	0.47	0.46	0.47	0.47
Fe ₂ O ₃	1.79	1.83	1.87	1.63	1.67	1.82	1.55	1.73	1.50	1.76
K ₂ O	3.93	3.54	3.68	3.71	3.96	3.86	3.01	4.04	4.93	3.93
MgO	0.60	0.80	0.74	0.61	0.60	0.60	0.60	0.60	0.59	0.60
MnO	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Na ₂ O	0.67	0.60	0.70	0.67	0.67	0.66	0.67	0.67	0.66	0.67
P ₂ O ₅	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
TiO ₂	0.93	0.95	0.93	0.91	0.94	0.93	0.93	0.93	0.93	0.94
LOI	4.60	4.30	4.30	4.60	4.30	4.30	3.50	4.60	2.50	4.60
Total	100.09	100.59	100.98	99.70	100.90	100.85	100.52	100.43	100.78	96.74

Appendix 2

See Tables 3 and 4.

Table 3 Physical properties determined for kiln-fired Sica Sica samples

Sica Sica unit NE deposit	Initial length (cm)	Drying shrinkage (%)		Fired length (cm)	Firing shrinkage (%)	Bending strength (N/mm ²)	Water absorption (%)
		24 h	48 h				
1	8.025	0.675	0.582	7.880	1.806	49.050	6.900
2	8.025	0.593	0.543	7.700	4.049	55.560	6.850
3	8.025	0.604	0.598	7.670	4.423	60.090	6.780
4	8.025	0.654	0.603	7.760	3.302	57.800	5.990
5	8.025	0.635	0.599	7.810	2.679	54.820	6.800
Media	8.025	0.632	0.585	7.760	3.251	55.460	6.660

Table 4 Physical properties determined for kiln-fired Vila Vila samples

Vila Vila unit SW deposit	Initial length (cm)	Drying shrinkage (%)		Fired length (cm)	Firing shrinkage (%)	Bending strength (N/mm ²)	Water absorption (%)
		24 h	48 h				
1	8.025	0.809	0.747	7.630	4.922	56.560	7.380
2	8.025	0.747	0.747	7.590	5.420	58.250	7.520
3	8.025	0.872	0.934	7.610	5.171	51.280	7.890
4	8.025	0.802	0.765	7.590	5.420	54.300	7.620
5	8.025	0.809	0.781	7.620	4.764	58.150	7.670
Media	8.025	0.807	0.794	7.608	5.139	55.700	7.610

Appendix 3

See Tables 5 and 6.

Table 5 Initial and final UTM coordinates of the geophysical lines

Points	UTM coordinates (initial)		Z (m)	UTM coordinates (final)		Z (m)	Lithology and electromagnetic values	Depth	Lithological units
	E	W		E	N				
G1	580691	8123479	4042	580777	8123254	4037	Fractured sandstones ($k = 4.1$); clays ($k = 5.5$); massive sandstones ($k = 9.6$)	7; 3.5; 19 m	Vila Vila
G2	580710	8123403	4227	580781	8123445	4215	Fractured sandstones ($k = 6.5$); wet sandstones ($k = 10.8$); clays ($k = 4.5$); massive sandstones ($k = 9.6$)	5; 3; 20; 23 m	Vila Vila
G3	580739	8123505	4019	580819	8123353	4029	Fractured sandstones ($k = 6.6$); wet sandstones ($k = 6.3$); massive sandstones ($k = 10.8$)	5; 4; 20 m	Vila Vila
G4	583779	8126427	4008	583710	8126269	4040	Fractured sandstones ($k = 5.4$); wet sandstones and siltstones ($k = 6.3$); massive sandstones ($k = 5.1$)	2.5; 3; 20 m	Sica Sica
G5	583669	8126297	4037	583773	8126242	4042	Fractured sandstones and siltstones ($k = 6.3$); clays ($k = 3$); massive sandstones ($k = 6.6$)	3.5; 1.5; 20 m	Sica Sica
G6	583746	8126263	4042	583823	8126263	4015	Fractured sandstones and siltstones ($k = 6.6$); massive sandstones and siltstones ($k = 5.7$); massive sandstones ($k = 5$)	3.5; 5; 12 m	Sica Sica
G7	583802	8126319	4028	583694	8126354	4029	Fractured sandstones and siltstones ($k = 6.6$); massive clays and sandstones ($k = 5.7$); massive sandstones ($k = 5$)	3.5; 5; 20 m	Sica Sica

Lithology and thickness are shown according to Ground Penetrating Radar results, modified table from the GPR report of Micaya, Ayala (2015)

Table 6 Initial and final UTM coordinates of the geophysical lines

Points	UTM coordinates (initial)		Z (m)	UTM coordinates (final)		Z (m)	Lithology and resistivity values	Depth	Lithological units
	E	N		E	N				
T1	580782	8123314	4245	580695	8123441	4250	Sandstones, siltstones and clays (30–80 Ω m); medium to coarse sandstones (81–1000 Ω m); sandstones and conglomerates (1001–6000 Ω m)	5; 20; 50 m	Vila Vila
T5	580736	8123482	4190	580822	8123360	4190	Sandstones, siltstones and clays (10–50 Ω m); sandstones and siltstones (51–550 Ω m); sandstones and conglomerates (551–9000 Ω m)	5; 7; 30 m	Sica Sica
T4	583827	8126228	4050	583696	8126303	4050	Sandstones, siltstones and clays (2–19 Ω m); clays (19–20 Ω m); siltstones (21–99 Ω m); sandstones (100–750 Ω m)	5; 10; 15; 20 m	Sica Sica
T3	583734	8126261	4050	583799	8126404	4035	Clays (1–24 Ω m); sandstones and siltstones (25–300 Ω m); sandstones (301–400 Ω m); sandstones and conglomerates (401–5400 Ω m)	15; 25; 12; 30 m	Sica Sica
T2	583722	8126366	4020	583876	8126325	4020	Medium to coarse sandstones (140–1900 Ω m); sandstones and conglomerates (1901–9000 Ω m)	20; 70 m	Vila Vila

Lithology thickness are shown according to Electrical Resistivity Tomography results, modified table from the ERT report of Micaya, Ayala (2013)

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