ORIGIN OF THE RIO CAPIM KAOLIN WITH BASIS ON OPTICAL (PETROGRAPHIC AND SEM) DATA

*Antônio Emídio de Araújo dos SANTOS Jr[1] and Dilce de Fátima ROSSETTI[2]**

(1) Universidade Federal do Pará/UFPa, Campus do Guamá S/N Belém-PA, Brazil. antonioemidio@hotmail.com
(2) Instituto Nacional de Pesquisas Espaciais/INPE, CP 515 São José dos Campos-SP 12245-970, Brazil. rossetti@dsr.inpe.br

(*) Corresponding author

DILCE DE FÁTIMA ROSSETTI
INSTITUTO NACIONAL DE PESQUISAS ESPACIAIS-INPE
CENTRO DE OBSERVAÇÃO DA TERRA
DIVISÃO DE SENSORIAMENTO REMOTO-DSR
RUA DOS ASTRONAUTAS 1758- JARDIM DA GRANJA--CP 515
SÃO JOSÉ DOS CAMPOS- CEP 12245-970 SÃO PAULO BRASIL
Fone: (012) 39456451 Fax: (012)39456488
e-mail: rossetti@dsr.inpe.br

(1) Universidade Federal do Pará/UFPa, Centro de Geociências, Campus do Guamá S/N Belém-PA. antoniojr@museu-goeldi.br
(2) Museu Paraense Emílio Goeldi/MPEG, Av. Perimetral, 1901, C.P.399, CEP. 66710-530. Belém-PA. rossetti@museu-goeldi.br

Origin of the Rio Capim Kaolin with basis on optical (petrographic and SEM) data

Antônio Emídio de Araújo Santos Jr.[1] and Dilce de Fátima Rossetti[2]

[1]*Universidade Federal do Pará/UFPa, Campus do Guamá S/N Belém-PA, Brazil.* *antonioemidio@hotmail.com*
[2]*Instituto Nacional de Pesquisas Espaciais/INPE, CP 515 São José dos Campos-SP 12245-970, Brazil.* *rossetti@dsr.inpe.br*

Abstract

The Ipixuna Formation (Late Cretaceous-?Early Tertiary) exposed in the Rio Capim area in northern Brazil was recently subdivided into three stratigraphic horizons, informally known as a lower soft kaolin unit, an intermediate kaolin unit, and an upper endured semi-flint kaolin unit. These units had their primary texture and composition strongly modified after deposition. Although characterization of the intermediate unit is problematic due to its poor preservation, petrographic and scanning electronic microscopic (SEM) investigation revealed many remaining features that allow differentiating the soft and the semi-flint kaolin deposits into two distinctive depositional sequences. The soft kaolin unit consists of well structured, sub-angular to sub-rounded, and locally angular, kaolinitized quartzose sandstones and kaolinitized sandstones that are interbedded with either laminated or massive pelites. These lithologies, composed by grains and lithic fragments related to felsic volcanic and meta-volcanic sources, as well as metamorphic and granitic rocks, had their texture and composition strongly modified, mostly likely during diagenesis, resulting in deposits with an actual wacky nature. Kaolinitization produced three types of kaolinites, categorized according to size and texture, as Ka, Kb and Kc kaolinites. Ka kaolinite, typical of the sandstones, consists of hexagonal to pseudohexagonal crystals 10-30 µm in diameter, and occurs as agglomerates of booklets or vermicular crystals that reach up to 400 µm in length. Kb kaolinite, dominating in the mudstones, consists chiefly of hexagonal and pseudohexagonal crystals averaging 1-3 µm in diameter that occur isolated, or as intergrowths of chaotic, face-to face or, less commonly, parallel to pseudo-parallel crystals. Kc kaolinite, abundant only in association with paleosols, displays hexagonal to pseudohexagonal crystals with regular sizes around 200 nm in diameter. In contrast, the semi-flint is attributed to a distinctive depositional unit formed by sediments from variable sources, but which appears to have had a significant contribution from the underlying soft kaolin. This is suggested by abundant sub-rounded to rounded sandstones with grains composed by homogeneous, dark brown masses of kaolinite that are strongly highlighted by films of iron oxides. Consequently, as opposed to the soft kaolin unit, the semi-flint is dominated by Kc kaolinite, related to enhancement of structural disorder during recycling, which acted together with pedogenesis in order to produce an endured deposit as typical of the semi-flint kaolin unit.

Keywords Petrology, Rio Capim kaolin, Cametá Sub-basin, kaolinite, origin, source area.

1. Introduction

The Ipixuna Formation that occurs in the Cametá Sub-basin, northern Brazil, is a geological unit of great economic interest for bearing one of the largest kaolin deposits in the world, the Rio Capim Kaolin. This unit has been investigated by several workers, who have mostly emphasized its sedimentologic, stratigraphic and geochemical aspects (Góes, 1981; Sousa, 2000; Santos Jr., 2002; Rossetti and Santos Jr., 2003; Santos Jr. and Rossetti, 2003). One important issue concerning to these deposits still open for debate is to decipher the origin of the kaolinite in order to better develop exploitation methods. Previous studies have suggested that the Rio Capim Kaolin is a product of deep weathering related to progressive drop of ground water affecting a single stratigraphic unit (Truckenbrodt et al., 1991; Kotschoubey et al., 1996; 1999; Costa and Moraes, 1998; Sousa, 2000). Despite these contributions, the origin of this kaolin deposits deserves to be further addressed, particularly considering newly available sedimentological and stratigraphic data (Santos Jr., 2002; Rossetti and Santos Jr., 2003; Santos Jr. and Rossetti, 2003). According to these authors, the kaolin deposits do not conform to a single stratigraphic unit. An unconformity separates the Ipixuna Formation into a lower soft kaolin unit and an upper hard kaolin unit, the latter consisting of flint-like fire clay with no plasticity when grounds up, known as semi-flint. Therefore, the soft and the semi-flint kaolin units have been attributed to distinctive depositional sequences. Additionally, a thin package of highly deformed deposits attributed to syn-sedimentary seismic activity is locally found between these two sequences, which are bounded by discontinuity surfaces that laterally merge into the sequence boundary (Rossetti and Santos Jr., 2003).

Taking this geological framework into account, a detailed characterization of the several types of kaolinite according to the stratigraphic horizons recognized within the Ipixuna Formation is needed to provide new information that can serve to the purpose of further discussing the origin of the Rio Capim Kaolin. Two types of kaolinite have been characterized in this area, consisting of a finer-grained kaolinite with high structural disorder, and a coarser-grained kaolinite with lower structural disorder that occurs mostly as booklets (Kotschoubey et al., 1999). According to these authors, these types of kaolinite reflect differences in lithology, with the finer-grained kaolinites forming from replacement of clay mineral in muddy deposits, while the coarser-grained kaolinites resulted from replacement of feldspar grains in sandy deposits.

This paper provides detailed petrographic and scanning electronic microscopic (SEM) descriptions of the kaolin units of the Rio Capim area (Fig. 1A) aiming to better understand the origin of the different types of kaolinites, as well as discuss their temporal relationships.

2. Geological framework

The Cametá Sub-basin is inserted in the eastern margin of the Marajó Graben System, which formed in association with the opening of the Atlantic Ocean during the Late Jurassic to Early Cretaceous (Azevedo, 1991; Galvão, 1991; Villegas, 1994; Costa et al., 2001). This sub-basin is filled by Cretaceous and Cenozoic deposits (Fig. 1B) that are up to 10 km thick. Cretaceous deposits are represented by the Breves (Aptian-Cenomanian) and the Limoeiro (Late Cretaceous) formations, while the Cenozoic deposits include the Marajó (Paleocene-Eocene) and Tucunaré (Pleistocene) formations. The majority of these deposits, formed in depositional settings ranging from fluvial to shallow marine (Villegas, 1994), occur in sub-surface. However, exceptional exposures are found along kaolin quarries in the Rio Capim area, where Upper Cretaceous-? Lower Tertiary deposits (Jupiassú, 1970) crops out, being known by the lithostratigraphic term of Ipixuna Formation. This unit is up to 40 m thick, consisting of a lower soft kaolin unit, an intermediate kaolin unit and an upper semi-flint kaolin unit (Fig. 2A), defined with basis of discontinuity surfaces (Fig. 2A and B). The intermediate kaolin unit occurs only locally, reaching up to 3 m thick. These deposits pinch out laterally, resulting in the direct superposition of the soft and the semi-flint kaolin units, which are bounded by an unconformity marked by well developed paleosol (Santos Jr. and Rossetti, 2003; Rossetti, 2004).

Despite the kaolinitized muddy appearance, many works have shown that the kaolin units in the Rio Capim area consist of lithologies varying from mudstones to conglomerates (Truckenbrodt et al., 1991; Kotschoubey et al., 1996; Santos Jr. and Rossetti, 2003, 2006; Rossetti and Santos Jr., 2003, 2006; Rossetti, 2004). The soft kaolin unit is well stratified, encompassing mostly sandy and muddy sedimentary facies attributed to tidal-influenced fluvial channel, tidal channel, tidal sand bar, sand flat and tidal flat/mangrove associated to a tidal estuarine system (Santos Jr. and Rossetti, 2003, 2006). The intermediate kaolin unit, composed of heterolithic deposits, as well as mudstones and sandstones, forms a horizon bounded by discontinuity surfaces, which contain a variety of soft sediment deformation (e.g., convolute fold, cuspide, ball-and-pillow fracture, fault) structures related to seismic activity (Rossetti and Santos Jr., 2003). The semi-flint kaolin unit, traditionally known as massive in nature, has been more recently considered to contain, at least in part, deposits that might be attributed to distributary channels and mouth bars associated to either a deltaic or wave-dominated estuarine setting (Rossetti and Santos Jr., 2006). According to these authors, these deposits also contain thin layers of quartzose sandstones related to transgressive lags.

3. Methods

This work was based on the petrographic and SEM analysis of 63 samples of kaolinitized sandstone, siltstone and mudstone collected from the Ipixuna Formation exposed along two kaolin quarries in the eastern Cametá Sub-basin (Fig. 1A). The samples were distributed along the profiles, aiming to properly record the three stratigraphic kaolin units, as well as their internal sedimentary facies.

All samples were impregnated with epoxy cements before starting the thin section preparation, given their soft and sometimes friable nature. After this procedure, the samples were cut and polished using a Logitech System. For the SEM analysis, small fragments and powered samples were mounted on stubs using silver tape. The use of these two types of sample aimed to analyze the texture, as well as the morphology of individual kaolinite crystals. After gold coating, the samples were analysed under a LEO 1450 VP electronic microscope from the Goeldi Museum, applying both secondary electrons and backscattering. The study of SEM images was combined with EDS analysis in order to help identifying the various mineral species.

4. Description of the kaolin units

Petrographic and SEM analyses revealed particular optical characteristics when the soft and the semi-flint kaolin units of the Ipixuna Formation were compared, with abrupt changes occurring at their boundaries. On the other hand, the intermediate unit could not be distinguished from the semi-flint kaolin and, for this reason, they will be described together herein. The following characterization of texture and mineralogy of the kaolin units takes into account only sandstones to mudstones, excluding the conglomerates that are abundant in the upper two kaolin units. Given the high degree of kaolinitization of the deposits, the lithologic classification provided below is far from representing a primary sediment composition. The most likely original sediment types are suggested in the discussions.

4.1. Soft kaolin

The soft kaolin unit is composed mainly by interbedded sandstone and pelite. The first represents the main lithology, and includes kaolinitized quartzose sandstones and kaolinitized sandstones. Kaolinitized quartzose sandstones (Fig. 3A-H) dominate in the lower portion of the soft kaolin unit. They vary from fine to coarse-grained and are, in general, moderately to well sorted, with grains that are sub-angular to sub-rounded, and locally angular. Their framework composition (Fig. 3A) consists of quartz (about 40-60%), with muscovite, feldspar, and lithics occurring secondarily (<5%). The remaining of the sandstones is composed by a kaolinitized "matrix", as well as large rounded kaolinitized clasts that are up to 2 cm in length. The quartz grains are monocrystalline and have their boundaries displaying different degrees of replacement by kaolinite. Where replacement was more intense, only relics of grains are found floating within masses of kaolinites. In addition to the monocrystalline quartz, there are a significant volume of limpid, either bipyramidal or cuneifor quartz grains with straight extinction, as well as numerous vacuoles and embayments filled by either kaolinite or kaolinitized mud. (Fig. 3B,C). Muscovite grains (Fig. 3D) are often bent and show anomalous birefringence due to partial replacement by large kaolinite crystals. Feldspars (Fig. 3E,F) are highly altered and replaced by kaolinite, but where grains are better preserved, albite twinning was observed. The lithics (Fig. 3G) consist mostly of mudstones, and secondarily of a mixture of muscovite, feldspar and quartz. These grains, in general larger than the average framework grains, display quartz that also displays bipyramidal or cuneiform shapes that are orientated according to a main direction coinciding with the maximum elongation axis of muscovite crystals, suggesting an incipient foliation. The interstitial space of the sandstones consists of a kaolinitized 'matrix" often containing enlarged areas, as well as ghosts of grains that were entirely kaolinitized (Fig. 3H). Where this "matrix" is less common, the framework grains display punctual contacts.

Upward in the sections, the sandstones become progressively less quartzose, given place to the kaolinitized sandstones. These sandstones are dominantly fine-grained, though medium and even coarse grain sizes are locally present. The contact between grains are punctual and, less commonly, concave-convex. The grains, moderately sorted and sub-angular to angular, consist mainly of either partly or entirely kaolinited grains (Fig. 4A, D). Quartz, feldspar, muscovite and lithic grains are locally present. The quartz is bipyramidal (Fig. 4E) or cuneiform, being internally limpid or, occurring most commonly as "ghosts" that contain only relicts of the original composition, consisting of numerous particles of a transparent mineral with low birefringence similar to quartz. The remaining parts of these grains are highly replaced by kaolinite. Partly or entirely kaolinitized grains display usually a bipyramidal shape similar to the quartz grains (Fig. 4F). The first shows many relicts of the original mineral composition, which are alike to those observed in the ghosts of quartz grains. A large volume of the kaolinitized grains, even those with bipyramidal shapes, displays numerous black inclusions (Fig. 4G) that are not present in the kaolinitized "matrix". Lithic grains might display composition alike the quarztoze sandstones described above or, more often, are composed by a dark kaolinitized massive material mixed with either limpid or partly kaolinitized bipyramidal quartz, feldspar and muscovite crystals (Fig. 4H).

The pelites (Fig. 5A,B), which increase in volume upward in the sections, consist of kaolinitized siltstones and mudstones that might be laminated forming heterolithic deposits. Large, well-rounded areas up to 0.5 mm in diameter with same composition than the surrounding deposits are locally present. Siltstones from the lower portion of the sections might display a high volume of quartz grains that are mostly angular. They also display prismatic, bipyramidal kaolinitized grains (Fig. 5B). Pelites with brown kaolinites are particularly widespread in the uppermost portion of the soft kaolin, where many fractures filled either by iron or clear kaolinites (Fig. 5C). These fractured pelites grade into reworked deposits displaying rounded clasts of similar composition than the surrounding pelites (Fig. 5D).

The above-described lithologies display three types of kaolinites, categorized according to size and texture, as Ka, Kb and Kc kaolinites. Ka kaolinite (Fig. 6A-C) consists of hexagonal to pseudohexagonal crystals 10-30 μm in diameter that occur as agglomerates of booklets (Fig. 6A) or vermicular (Fig. 6B) shapes that reach up to 400 μm in length. Either single or composite booklets are present, the latter being formed by a set of laterally coalescing single booklets. Euhedral, elongated prismatic kaolinite crystals 1-3 μm of length growth out from the booklet sheets (Fig. 6C). Many Ka kaolinites display anomalous birefringence and grade into muscovite grains. Kb kaolinite (Fig. 6D-G) consists of hexagonal and pseudohexagonal crystals averaging 1-3 μm in diameter

(Fig. 6D) that occur isolated, as intergrowths of chaotic, face-to face (Fig. 6E) or, less commonly, parallel to pseudo-parallel (Fig. 6F) crystals similar to the ones described by Pickering and Hurst (1989). This type of kaolinite might occur also arranged as booklets that are 5-10 µm in length. Lozenge kaolinite crystals are intergrown with this type of kaolinite and crudely developed single rectangular booklets are common (Fig. 6G). Kb kaolinite is either distributed homogeneously in the thin sections, or form masses containing agglomerates of Ka kaolinites dispersed within them. In addition, part of this kaolinite occurs in association with bipyramidal crystal ghosts, as well as kaolinitized grains of the framework. Kc kaolinite (Fig. 6H) also displays hexagonal to pseudohexagonal forms, but in this case the crystals have regular sizes around 200 nm in diameter.

Amongst all the kaolinite types described above, the sandstones bear the largest volume of Ka kaolinites, with Kb kaolinites occurring subordinately, and Kc kaolinites being absent or, less commonly, rare. Ka kaolinites often form aggregates of sand grain sizes. Part of this kaolinite is also dispersed in the kaolinitized "matrix", in association with Kb kaolinites. On the other hand, Kc kaolinites occur consistently dispersed over the other two types of kaolinites. The pelites are dominated by Kb kaolinites, with Ka kaolinites being either rare or absent. Kc kaolinites are more frequent in this lithology than in the sandstones. Its volume increases progressively upward, reaching a maximum in the fractured pelites with brown kaolinites that occur near the contact with the discontinuity surface at the top of the soft kaolin.

4.2. Intermediate and semi-flint kaolin units

In addition to conglomerates, these units are dominated by sandstones, mudstones and heterolithic deposits. As previously mentioned, the latter is restricted to the intermediate unit, occurring as slightly undulating or highly folded deposits. Kaolinitized, well rounded, moderately sorted, fine-grained to silty sandstones alternate with massive mudstones, forming well-defined laminations. The intermediate unit is, in general, soft, becoming harder only in its upper portion in association with paleosols, but even so, it is softer than the semi-flint kaolin. Its base displays Kb, and more rarely Ka, kaolinites, both pervasively draped by Kc kaolinites (Fig. 7A). The volume of the latter increases substantially upward (Fig. 7B), where pedogenetic features are present.

The intermediate kaolin is sharply overlain by massive, endured mudstones and sandstones of the semi-flint kaolin unit. The mudstones (Fig. 7C) are homogeneous and consist of yellowish-brown Kc kaolinite and, secondarily, Kb kaolinites, with the first increasing in volume upward. The mudstones from the top of the semi-flint unit might be entirely composed by Kc kaolinites. They also show numerous irregular fractures and fenestrae of variable sizes (Fig. 7C) that are filled by clear kaolinites.

Two types of sandstones occur in the intermediate and semi-flint units: quartz-sandstone and kaolinitized sandstone. Quartz-sandstones, which occur only in association with layers attributed to transgressive lags (Rossetti and Santos Jr., 2006), are very friable, contrasting with the overall surrounding endured, kaolinitized deposits. These sandstones are moderately to well sorted, well rounded, and vary from fine to medium grain sizes. Kaolinitized sandstones are mostly moderately- to poorly-sorted, with very fine to medium grains sizes that are, in general, sub-rounded to rounded (Fig. 7D). The grains, which display punctual and, very rarely, concave-convex contacts, consist of a homogeneous mass of dark brown kaolinite composed dominantly by Kc kaolinites (Fig. 7E), with only relicts of Kb kaolinites. Their boundaries are strongly highlighted by coatings of iron oxide, present even between grains. The interstitial space was completely filled by cement of clear kaolinite. Samples displaying this characteristic revealed to contain well-developed booklets of kaolinites (i.e., Ka kolinite), as well as iron oxides and halloysite. The iron oxides form spheres or regular size (Fig. 7F), while the halloysite forms an interlaced network of either tabular (Fig. 7G) or elongated, hairy (Fig. 7H) crystals. Nevertheless, the SEM microscopic analysis also revealed that a great part of the interstitial space consists of Kc kaolinites. Eventually, the framework grains might be fractured and filled by the clear kaolinite.

5. Discussion

Taking into account the high degree of kaolinitization of the studied deposits, reconstructing their primary nature, as well as determining the several phases of kaolinite formation, are issues hard to be approached. Previous studies have proposed granitic and metamorphic sources throughout the kaolin deposits of the Ipixuna Formation (Nascimento and Góes, 2005), with kaolinite resulting from replacements of feldspar grains and muddy matrix from arkosic deposits during progressive deep weathering (Truckenbrodt et al., 1991; Kotschoubey et al., 1996, 1999).

In general, determining sandstone provenance is one of the most problematic issues in sedimentary geology. This is because one must consider the influence of various factors (e.g., type of rock, relief, climate, tectonics, flow dynamics, depositional environment) acting in the source area, as well as during sediment transportation, deposition and evolution after burial (Folk, 1974; Basu, 1975; Young, 1975) in order to discuss sediment sources. In addition to all these factors, the present location of the studied deposits in a tropical area, further contributed to modify their primary characteristics due to weathering. Despite this high complexity, the detailed optical (i.e., petrographic and SEM) information presented herein, when analysed within a faciological and stratigraphic framework, allow reviewing the available interpretations concerning to the origin of the Rio Capim Kaolin.

5.1. Composition and genesis of the soft kaolin unit

The great thickness, added to the well stratified nature, of the soft kaolin unit of the Ipixuna Formation, have long been used to propose an origin for the kaolin related to *in situ* alteration of feldspar grains from arkosic deposits and clay minerals from mudstones due to deep weathering, beyond the influence of surface soil formation (Kotschoubey *et al*., 1996; 1999). Determining whether deep weathering or diagenesis was responsible for kaolinitization is an issue opened for debate. Optical observations concerning to the three categories of kaolinites described herein confirm an origin related to kaolinitization of various types of material. The enhancement of Kc kaolinite towards the top unconformity is taken as a good evidence of a genesis related to weathering and, possibly, soil formation. The presence of many fractures filled by clear kaolinite is possibly related to the action of roots. Therefore, the Kc kaolinite seems to have been formed, at least in great part, by replacement of Ka and Kb kaolinites, as suggested by its occurrence consistently over Ka and Kb kaolinites. This is also suggested by the inverse proportion in the volume of Kc kaolinites with respect to the other kaolinites. On the other hand, the increased abundance of Ka and Kb kaolinites in mudstones and sandstones, respectively, is a good indication that the first resulted, at least in great part, from replacement of other clay minerals, while the second is chiefly related to replacement of sand grains. These mineral transformations predate the formation of Kc kaolinites, suggesting that Ka and Kb kaolinites had an origin unrelated to weathering associated to the top unconformity, being most likely formed by contact with intrastratal fluids during a previous burial.

The quartzose sandstones display regular quartz grains derived either from granitic or metamorphic rocks, or even both. The upward gradation from quartzose sandstones into kaolinitized sandstones attests to a change in sand composition. The almost complete disappearance of regular quartz grains upward in the soft kaolin unit is taken as further evidence to support diversified sediment source. The presence of monazite and topaz points to igneous contribution (Nascimento and Góes, 2005). However, if only a granitic source would be considered, the volume of quartz grains should have remained constant even if the grain size decreased (Tortosa et al., 1991). Despite the overall increase in the abundance of finer-grained sandstones upward in the soft kaolin unit, the fact that many intervals with kaolinitized sandstones are of same grain size as the quartzose sandstones led to suspect of a possible change in sediment source. The presence of heavy minerals such as kyanite and staurolite confirms a metamorphic contribution for these sediments (Nascimento and Góes, 2005). The domain of monocrystalline, instead of polycrystalline, quartz grains are more typical of high degree of metamorphism (Yong, 1975). On the other hand, the abundance of bipyramidal quartz grains with straight extinction, embayments and vacuoles attests the presence of sediments derived from felsic volcanic rocks (e.g., Folk, 1974; Scholle, 1979). Lithic fragments containing bipyramidal quartz crystals parallel to muscovites suggest either an incipient foliation or primary bedding, leading to invoke a contribution from either fine-grained volcaniclastics or volcanic rocks with a certain degree of metamorphism.

The prevalence of bipyramidal quartz, either as grains or crystals within lithic grains, conforms to a great influence of felsic volcanic fragments. The kaolinitized grains displaying bipyramidal or cuneiform shapes similar to quartz, but which have been replaced either entirely or partly by kaolinite, might record grains belonging to the silica group, but of a different species more suitable for replacement. Ghosts of grains with bipyramidal shape led to suspect on the presence of cristobalite. As quartz, cristobalite is a mineral formed by sheets of tetrahedra pointing alternately up and down, resulting in a bipyramidal shape. In addition, this mineral is usually found in association with volcanic rocks (e.g., Nesse, 1991), thus being consistent with the proposed. Unfortunately, because only relicts of this mineral are preserved, its optical characterization was not enough to draw any further conclusions. The numerous black inclusions associated to these grains are taken as residues left behind during dissolution, followed by replacement by kaolinite, an interpretation consistent with the fact that this type of material is absent in the kaolinitized matrix.

If the foregoing interpretation is correct, then a great portion of the kaolinitized sandstones is formed by lithic grains of volcanic sources. In fact, it is possible that much of the bipyramidal quartz and cristobalite (?) of the sandstone framework are, in fact, crystals from lithic grains that were left behind during kaolinitization. This is suggested with basis on the presence of many areas of the kaolinitized “matrix” with ghosts of grains with floating crystals within. Thus, part of the “matrix” is in fact a pseudomatrix formed by replacement of the framework grains by kaolinite. Kaolinitization of the framework grains was pervasive, affecting not only lithic grains, but also feldspar, muscovite and, less intensely, granitic and metamorphic quartz.

Kaolinitization of framework grains produced large kaolinite crystals as agglomerates of booklets, which form part of the Ka kaolinite. The crudely developed, large, rectangular booklets probably record kaolinitized feldspar grains. This is suggested because this shape is similar to many feldspar grains that are still preserved in the framework. Large kaolinite booklets resulted also from replacement of muscovite, which is indicated by the fact that many large booklets displaying anomalous birrefrigence grade into muscovites. The presence of large kaolinite crystals associated with both feldspar and muscovite grains are probably due to the larger volume of Al, as well as Si and O, available from alteration of these minerals. Lozenge kaolinite crystals intergrown with Ka booklets suggest a phase of kaolinite precipitation postdating the formation of booklets.

Despite the fact that most of the Kb kaolinite resulted from kaolinitization of clay minerals from mudstones, as previously stated, this work shows that part of it derived also from alteration of framework grains. This is revealed by the occurrence of this type of kaolinite in association with ghosts of quartz and cristobalite (?) grains and crystals from lithic fragments. In summary, although the largest volume of Kb kaolinite resulted from replacement of mudstone layers, a considerable amount of this kaolinite resulted also from replacement of framework grains. In this case, dissolution of SiO_2 provided elements that combined with Al from circulating fluids in order to form Kc kaolinites.

5.2. Composition and genesis of the semi flint kaolin unit

Hard, semi-flint kaolin deposits resembling the ones from the Rio Capim area have been described in association with many other kaolin deposits worldwide. The origin of these endured kaolin overlying soft kaolin deposits have been a matter of great debate (e.g., Bates 1964; Hurst and Bosio, 1975; Murray and Partridge, 1982; Truckenbrodt et al. 1991; Murray and Keller, 1993; Yuan and Murray, 1993; Chen et al., 1997; Kotschoubey et al., 1999; Montes et al., 2002). These authors have often related the hard kaolin deposits to kaolinites with high degree of structural disorder. The action of inorganic acids and microbes in soils and weathering crusts is known to cause the destruction of clays, with the consequent decrease of structural disorder (Hurst and Pickering Jr., 1997; Hradil and Hostomsky, 2002). Other workers have attributed the origin of the semi-flint kaolin to clay flocculation in the presence of alkaline seawater (Keslller, 1956; Schofield and Sampson, 1954; Pickering and Hurst, 1989; Dombrowski, 1993).

The genesis of the semi-flint kaolin in the Rio Capim area has been interpreted to be closely related to the underlying soft kaolin, with the hard kaolin recording the uppermost portion of progressive downward weathering (e.g., Sousa 2000). The origin of the semi flint kaolin has been also related to *in situ* precipitation of amorphous kaolinite by descending solutions under influence of organic acids, combined with the action of bacterias (Kotschoubey et al., 1996). In the following, optical data are integrated with sedimentological and stratigraphic information recently available in the literature in order to propose that the semi-flint and the soft kaolin units had different depositional and evolutionary histories. In addition, it is stated that the Kc kaolinite, rather than representing *in situ* precipitation, resulted from multiple origins.

A significant part of the Kc kaolinite in the semi flint kaolin unit results from pedogenetic processes. Likewise the soft kaolin unit, this is suggested by an overall increase in the volume of Kc kaolinite relative to Ka and Kb kaolinites upward in the semi flint kaolin. As our unpublished work focusing on oxygen and hydrogen isotopes demonstrates that the Kc kaolinite has values that contrast with modern soil waters, it is proposed that this type of kaolinite was most likely formed under influence of the paleosol developed in association with the unconformity at the top of the Ipixuna Formation (Rossetti, 2004).

Despite the pedogenetic influence, it is possible that the Kc kaolinite from the semi flint kaolin unit had other origins. An important information to recall from previous work is the presence of an unconformity between the soft and the semi flint kaolin units, implying to state that these deposits correspond to distinctive depositional sequences (Santos Jr., 2002; Rossetti and Santos Jr., 2003; Santos Jr. and Rossetti, 2003). An ongoing study focusing on heavy minerals comparing these units attests to mineralogical assemblages having different textural characteristics. Hence, there is an abrupt increase in grain roundness when crossing the basal unconformity, which led to suspect that part of the semi-flint kaolin might have been formed by reworking of the underlying soft kaolin.

A large volume of kaolinitized, mud-supported breccias and conglomerates has been reported in these deposits, which is consistent with intense sediment reworking (e.g., Kotschoubey et al. 1996; Santos and Rossetti, 2003; Rossetti and Santos Jr., 2006). In addition, according to the latter authors, an important part of the semi-flint kaolin encompasses deposits representative of mouth bar deposits, requesting a primary sandy composition. This study revealed that even the muddier hard kaolin is, at least in great part, composed by sand grain sizes, and not muds as originally thought. The well to moderate grain roundness, as well as the iron-oxide coatings predating mechanical compaction, as suggested by their presence even where grains are in contact, conform to deposition of this kaolin as sands. It is suspected that the sands might have been produced by reworking of the underlying soft kaolin unit. Together with the heavy mineral assemblage, this is suggested because, as opposed to the underlying kaolinitized sandstones from the soft kaolin unit, these sandstones are formed by grains consisting exclusively of completely homogeneous masses of dark brown Kc kaolinites. As the uppermost part of the soft kaolin was exposed to weathering during development of a sequence boundary between the soft and the semi flint kaolin units (Rossetti, 2004), the formation of Kc kaolinites, represented by interlocking of crystals <200 nm in diameter, was favored. Reworking of this material in a new depositional setting (in this instance, deltaic mouth bars) might have resulted in sandstones composed by rounded grains of kaolin already displaying a certain degree of hardness promoted by the prevalence of Kc kaolinites.

The presence of distinctive clear Kc kaolinite filling up the interstitial spaces of the sandstones, as well as the fractures, indicates that the semi flint kaolin was further endured due to cementation. The fact that the SEM analysis revealed the presence of halloysite and Ka kaolinites in samples displaying clear kaolinite led to argue that this cement is actually represented by a mixture of these minerals. In particular, it has been claimed that the presence of halloysite might contribute to increase significantly the hardness of kaolin deposits due to the intricate crystals intergrowth (e.g., Grant, 1963; Bates, 1964; Osborne et al., 1994). In this instance, the volume of halloysite is probably low, but they occur only in the semi-flint kaolin. The occurrence of this mineral as cement in kaolin deposits is usually related to pedogenesis (e.g., Keller, 1977, 1982). Halloysite precipitating together with Ka and Kc kaolinites in the interstitial porosity probably have contributed to endure the semi-flint kaolin unit.

In addition of a derivation from the underlying soft kaolin unit, the sediments that gave rise to the semi-flint had a contribution directly from metamorphic rocks. This is suggested also by an ongoing study that reveals the presence of euhedral staurolite and kyanite, as well as the occurrence of hornblende, with no evidence of dissolution, characteristics not present in the underlying soft kaolin unit. Furthermore, a sedimentary source is proposed for the quartz sandstones, which were related to intense reworking associated with marine flooding surfaces (Rossetti & Santos Jr., 2006).

6. Final remarks

The present optical studies allow attributing the soft and the semi-flint kaolin units to distinctive depositional sequences. In addition to the unconformity mapped between these sequences, the recognition of different sources for the sediments is consistent with this interpretation. Furthermore, the kaolinite from these deposits had distinctive origins, as great part of the soft kaolin represent kaolinitization of framework grains of sandstones and replacement of other clay minerals from mudstones. Kaolinitization was so intense that modified most of the primary composition, but as shown in the foregoing discussion, detailed optical studies revealed many relicts of the original texture suggesting that the kaolinitized sandstones were formed by lithic grains of felsic volcanic, as well as volcaniclastics or meta-volcanic rocks. Diagenesis of these sandstones promoted significant compositional changes, with strong kaolinitization of the framework grains. Lithic grains, as well as grains having a probable cristobalite composition, were more suitable for replacement than quartz grains. The kaolinitization process contributed to produce a deposit with a large volume of pseudomatrix, which gave them the actual wacky composition. The abundance of relicts and ghosts of grains, as well as enlarged areas between grains that appear to float in the matrix, however, led to the conclusion that these are artificial wackes produced during kaolinitization.

The upward almost disappearance of regular quartz grains in the soft kaolin unit is explained by a change in both sedimentary conditions and sediment sources, a situation that might have been favored by the estuarine nature of the depositional setting, as proposed for these deposits (Rossetti and Santos Jr., 2003; Santos Jr. and Rossetti, 2003). Hence, the quartzose sandstones from the base of the sections might record higher energy flows associated to the initial transgression of the estuarine system. During this process, unstable grains have higher potential to be lost due to the strong reworking by tidal currents and waves, which favors deposition of sands rich in quartz grains at the estuary axis. As the estuary is filled with sediment, there is a greater interaction of marine and fluvial flows, with the latter dominating in inner estuarine areas. The deposits located in the middle and upper portions of the studied sections formed in a variety of tidal depositional settings typical of inner and middle estuarine areas. The sediment in these settings derived mainly from fluvial inflows, resulting in sandstones with composition of the framework grains that varied with relation to the quartzose sandstones. Diagenesis of these deposits led to an intense kaolinitization, but with preservation of primary structures. Burial promoted the replacement of sandstones and mudstones by Ka and Kb kaolinites. Kc kaolinites formed later on by replacement of Ka and Kb kaolinites in association with pedogenesis related to the development of the unconformity that bounds the top of the soft kaolin unit.

The semi flint kaolin, on the other hand, resulted from sediments reworked from the underlying soft kaolin deposits, which were mixed with an additional nearby metamorphic source. This would have brought Kc kaolinites from the upper, slightly endured portion of the soft kaolin. The reworked sediment would have been reduced to sand grain sizes, adopting a dirt appearance during transportation, and becoming coated by iron oxide. Weathering acting during transport contributed to further endure the kaolin grains. Following deposition, additional Kc kaolinite was formed throughout the semi flint kaolin due to pedogenetic processes associated to the unconformity that marks the top of the Ipixuna Formation. Further Kc kaolinite was introduced by cementation of sandstones and filling of fractures.

Despite the sharp boundaries and the softer nature, the intermediate unit displays sedimentological features with more affinity to the semi-flint kaolin than to the soft kaolin unit. The intermediate and the semi-flint kaolin units also have comparable heavy mineral characteristics, as well as prevalence of Kc kaolinites. The data presented herein, however, was not enough to decide if the intermediate kaolin is the remaining of a distinctive depositional unit or part of the semi-flint kaolin unit, as previously pointed out (Rossetti, 2004).

Acknowledgments

This paper was financed by the CNPq (Grant #474978/2001-0). Logistic support was provided by the Goeldi Museum. The Imery-Rio Caulim Capim-IRCC and Pará-Pigmentos S/A-PPSA are acknowledged for the permission to access the kaolin quarries. The geologists Carlos Henrique L. Bastos and Sá Pereira are thanked for the companionship and discussions in the field. The authors are also thanked to the engineer in chief of the IRCC, Leonardo Fonseca, for providing logistic support during fieldwork.

References

Azevedo, R.P., 1991. Tectonic Evolution of Brazilian Equatorial Continental Margin Basins. PhD thesis, Royal School of Mines Imperial College, London, 412 pp.

Basu, A., 1975. Petrology of Holocene fluvial sand derived from plutonic source rocks: implication to provenance Interpretation. MSc thesis, Indiana University, Bloomington, 138 pp.

Bates, B.F., 1964. Geology and Mineralogy of the Sedimentary kaolins of the Southeastern United States. A review: Clay and Clay Minerals. In: W.F. Bailey (Ed.), Procedures of the Twelfth Nacional Conference, 1963. Macmillan, New York, pp. 177-194.

Chen, P.Y., Lin, M.L., Zheng, Z., 1997. On the origin of the name kaolin and the kaolin deposits of the Kauling and Dazhou areas, Kiangsi, China. Applied Clay Science 12, 1-25.

Costa, J.B.S., Bemerguy R.L., Hasui, Y., Borges, M.S., 2001. Tectonics and paleogeography along the Amazon River. Journal of South American Earth Sciences 14, 335-347.

Costa M.L., Moraes E.L., 1998. Mineralogy, geochemistry and genesis of kaolins from the Amazon region. Mineralium Deposita 33, 3-297.

Dombrowski, T., 1993. Theories of origin for the Georgia Kaolins: A review. In: H. Murray, W. Bindy, C. Harvey (Eds.), Kaolin genesis and Utilization, Clay Mineral Society Special Publication 1, pp. 75-98.

Folk, R.L., 1974. Mineral composition of sedimentary rocks. In: Petrology of Sedimentary rocks. Hemphill Publishing Company. Austin, Texas, pp. 65-145.

Galvão, M.V.G., 1991. Evolução Termodinâmica da Bacia do Marajó, Estado do Pará, Brasil. MSc thesis, Universidade de Ouro Preto, Ouro Preto, 193 pp.

Góes, A.M., 1981. Estudo Sedimentológico dos Sedimentos Barreiras, Ipixuna e Itapecuru, no Nordeste do Estado no Pará e Noroeste do Maranhão. MSc thesis, Universidade Federal do Pará, Belém, 55 pp.

Grant, W.H., 1963. Weathering of Stone Moutain granite: Clay and Clay Minerals, 11th Conference, Pergamon Press, New York, pp. 65-74.

Hradil, D., Hostomský, J., 2002. Effect of composition and physical properties of natural kaolinitic clays on their strong acid weathering rates. Catena 49, 171-181.

Hurst V.J., Bosio N.J., 1975. Rio Capim Kaolin deposits, Brazil. Economic Geology 70, 990-992.

Hurst, V.J., Pickering Jr., S.M., 1997. Origin and classification of coastal plain kaolins, southeastern USA, and the role of groundwater and microbial action. Clays and Clay Minerals 45, 272-285.

Jupiassú, A.M.S., 1970. Madeira Fóssil – Humiriaceae de Irituia, Estado do Pará. Boletim do Museu Paraense Emilio Goeldi 14, 1-12.

Keller, W.D., 1977. Scan electron micrographs of kaolin colleted from diverse environments of origin-IV. Georgia kaolin and kaolinizing source rocks. Clay and Clay Minerals 25, 311-345.

Keller, W.D., 1982. A most diverse rock in genesis, texture, physical properties, and uses. Geological Society of America Bulletin 93, 27-36.

Kesler, T.L., 1956. Environment and origin of the Cretaceous kaolin deposits of Georgia and South Carolina. Economic Geology 51, 541-554.

Kotschoubey, B., Duarte, A.L.S., Truckenbrodt, W., 1999. Cobertura bauxítica e origem do caulim do Morro do Felipe, Baixo Rio Jari, Estado do Amapá. Revista Brasileira de Geociências 29, 331-338.

Kotschoubey, B., Truckenbrodt, W., Hieronymus, B., 1996. Depósitos de caulim e argila semi-flint no nordeste do Pará. Revista Brasileira de Geociências 26, 71-80.

Montes, C.R., Melfi, A.J., Carvalho, A., Vieira-Coelho, A.C., Formoso, M.L.L., 2002. Gênesis, mineralogy and geochemistry of kaolin deposits of the Jarí River, Amapá State, Brazil. Clays and Clay Minerals 50, 494-503.

Murray, H.H., Keller, W.D., 1993. Kaolins, Kaolins and Kaolins. In: H. Murray, W. Bundy, C. Harvey (Eds), Kaolin Genesis and Utilization, Clay Mineral Society Special Publication 1, 1-24.

Murray, H.H., Partridge, P., 1982. Genesis of rio Jarin kaolin. In: H. Van Olphen, F. Veniale (Eds), Developments in Sedimentology, Elsevier, Amsterdam 35, 279-291.

Nascimento, M.S., Góes, A.M., 2005. Distribuição estratigráfica e proveniência de minerais das formações Ipixuna e Barreiras, região do Rio Capim, Sub-Bacia de Cametá, Estado do Pará. Revista Brasileira de Geociências 35, 49-58.

Nesse, W.D., 1991. Introduction to optical mineralogy. Second edition. Oxford University Press, Oxford, 335 pp.

Osborne, M., Haszeldine, R.S. and Fallick, A.E., 1994. Variation in Kaolinite morphology with grouwth temperature in isotopiclly mixed pore-fluids, Brent Group, UK North Sea. Clay Minerals 29, 591-608.

Pickering, S.M., Hurst, V.J., 1989. Commercial Kaolins in Georgia. Occurrence, Mineralogy, Origin, Use. Geological Society Guidebooks 9, 29-75.

Rossetti, D.F., 2004. Paleosurfaces from northeastern Amazonia as a key for reconstructing paleolandscapes and understanding weathering products**.** Sedimentary Geology 169, 151-174.

Rossetti, D.F., Santos Jr., A.E., 2003. Events of soft sediment deformation and mass failure in Upper Cretaceous estuarine deposits (Cametá Basin, northern Brazil) as evidence for seismic activity. Sedimentary Geology 161, 107-130.

Rossetti, D.F., Santos Jr., A.E.A., 2006. Analysing the origin of the Upper Cretaceous-?Lower Tertiary Rio Capim semi flint (Pará State, Brazil): under a sedimentologic perspective. Sedimentary Geology 186, 133-144.

Santos Jr., A.E.A., 2002. Reconstrução Paleoambiental e Estratigráfica de Depósitos Cretáceos e Terciários Expostos na Borda Sudeste da Sub-Bacia de Cametá, Norte do Brasil. MSc thesis, Universidade Federal do Pará, Belém, 131 pp.

Santos Jr., A.E.A., Rossetti, D.F., 2003. Paleoambiente e estratigrafia da Formação Ipixuna, Área do Rio Capim, Leste da bacia de Cametá. Revista Brasileira de Geociências 33, 313-324.

Santos Jr., A.E.A., Rossetti, D.F., 2006. Depositional model of the Ipixuna Formation (Late Cretaceous-?Early Tertiary), Rio Capim Area, northern Brazil. Latin American Journal of Sedimentology and Basin Analysis (in press).

Schofield, R.K., Sampson, H.R., 1954. Flocculation of kaolinite due to the attraction of oppositely charged faces. Faraday Society Discussion 18, 135-145.

Scholle, P.A., 1979. A color illustrate guide to constituents, textures, cements and porosity of sandstones and associated rocks. American Association of Petroleum Geologist, Tulsa, 201 pp.

Sousa, D.J.L., 2000. Caracterização Geológica, Mineralógica, Química e Física do Caulim da RCC - Rio Capim Caulim (PA). MSc thesis, Universidade Federal do Pará, Belém, 116 pp.

Tortosa, A., Palomares, M., Arribas, J., 1991. Quartz grain types in Holocene deposits from the Spanish Central System: some problems in provenance analyis. In: A.C. Morton, S.P. Todd, P.D.W. Haughton (Eds.), Development in Sedimentary Provenance Studies, Geological Society Special Publication 57, 47-54.

Truckenbrodt, W., Kotschoubey, B., Schellmann, W., 1991. Composition and origin of the clay cover on North Brazilian laterites. Geologische Rundschau. 80, 591-610.

Villegas, J.M.C. 1994. Geologia Estrutural da Bacia do Marajó. MSc thesis, Universidade Federal do Pará, Belém, 119 pp.

Young, S.W., 1975. Petrography of holocene fluvial derived from regional metamorphic source rocks. MSc thesis, Indiana University, Bloomington, 93 pp.

Yuan, J., Murray, H.H., 1993. Mineralogical and physical properties of the Maoming Kolin from Guandong Province, South China. Clay Mineral Society Special Publication 1, 249-260.

Figures

Fig. 1. A) Location of the study area in the eastern Cametá Sub-Basin, Marajó Graben System, with indication of the two studied quarries, the IRCC and PPSA. SBC=Cametá Sub-Basin, SBL=Limoeiro Sub-Basin and SBM=Mexiana Sub-Basin. B) Lithostratigraphic chart of the Cametá Sub-Basin.

Fig. 2. A) Lithostratigraphic profiles representative of the Ipixuna Formatin in the studied quarries. B) General view of the Ipixuna Formation in the PPSA quarry, illustrating the soft kaolin and the semi flint kaolin units separated by a sharp discontinuity

surface, attributed to an unconformity. Note also the unconformity at the top of the semi flint kaolin, which is overlain by Tertiary deposits.

Fig. 3. Kaolinitized quartzose sandstone, representative of the lower portion of the soft kaolin unit, illustrating: A) a broad view of the framework dominated by monocrystalline quartz grains; B,C) quartz grains with bipyramidal or cuneiform shapes, as well as vacuoles and embayments filled by kaolinite; D) muscovite grain partly replacement by kaolinite; E,F) feldspar grain partly replaced by kaolinite (note the albite twinning and prismatic shape); G) a lithic fragment (arrows) composed by muscovite, cuneiform quartz and a kaolinite, the latter resulting from replacement of other mineralogical constituents of the grain (note the that the quartz crystals-Qz are broadly aligned parallel to the maximum elongation axis of the muscovite-Mu); H) ghosts of totally kaolinitized grains (arrows) with texture similar to the matrix. (A-E and G=crossed polars; F= SEM, secondary electrons; H=parallel polars).

Fig. 4. Kaolinitized sandstone, representative of the middle and upper portion of the soft kaolin unit. A-B) A view of an intensely kaolinitized framework with parallel (A) and crossed polars (B), where the contours of well rounded grains are still preserved (hatched lines and arrows in A and B, respectively). Note many relics of a mineral (cristobalite?; light color) not replaced by kaolinite. C) SEM view (back scatter) of the framework, highlighting two, well rounded, kaolinitized sand grains (hatched lines). D) A detail of a a grain completely replaced by Kb kaolinites crystals (SEM, back scatter). E) Bipyramidal quartz within a kaolinitized framework with two ghosts of sand grains

(SEM, back scatter). F) Bipyramidal-shaped cristobalite (?; circles) floating within a kaolinitized “matrix”, which might represent either individual euhedral grains or crystals from lithic grains that were left behind during kaolinitization (crossed polars). G) Kaolinitized bipyramidal grains (arrows), with numerous black inclusions, probably a product of replacement of the grains by kaolinite (crossed polars). H) A detail of a large, kaolinitized lithic grain with relics of pyramidal quartz and muscovite crystals (crossed polars).

Fig. 5. Deposits from the top of the soft kaolin unit. A) A general view of massive, kaolinitized mudstone with a few, disperse grains of quartz. B) Heterolithic deposits formed by alternating laminae of light brown to greenish brown siltstone (dark color) and very-fine grained sandstone (light color). Note the relicts of prismatic and/or bipyramidal quartz grains (circles) within the siltstone. C) Kaolinitized mudstone from a paleosol horizon at the top of the soft kaolin unit. Note the several areas cemented by clear kaolinite, related to fractures and/or roots (arrows). D) A reworked deposit from the top of the paleosol horizon, forming sandstone cemented by clear kaolinite (arrows) and iron oxides (black color).

Fig. 6. Kaolinite from the soft kaolin unit. A) Agglomerate of Ka kaolinites, consisting of booklets of hexagonal to pseudohexagonal crystals up to 30 μm in diameter. B) U-shaped, vermicular Ka kaolinite. C) A booklet of Ka kaolinite with superimposed prismatic rectangular crystals that grow out from the kaolinite sheets. Note the local agglomerate of Kc kaolinite in the lower left side of the picture. D) Kb kaolinite

composed by hexagonal and pseudohexagonal crystals averaging 1-3 μm in diameter. E) Kb kaolinite, consisting of crystals with face-to face arrangement (circle). F) Kb kaolinite, consisting of crystals with parallel to pseudo-parallel arrangement (circle). G) A crudely developed booklet of kaolinite, attributed to result from replacement of a feldspar grain. H) Kc kaolinite, consisting of hexagonal to pseudohexagonal crystals with regular size around 200 nm in diameter, typical of the paleosol horizon from the top of the soft kaolin unit.

Fig. 7. Endured mudstones and sandstones representative of the intermediate and semi-flint kaolin units. A,B) Texture of kaolinites from the lower portion of the intermediate kaolin unit, where Kb kaolinites occur in association with Kc kaolinites, with the volume of the latter increasing significantly upward (B) in association with a paleosol horizon.(SEM, secondary electrons). C) Kaolinitized mudstone of the semi flint unit, characterized by a massive texture and displaying fractures and fenestrae filled by clear kaolinite (arrows) (parallel polars). D) Kaolinitized sandstone of the semi flint unit, consisting of sub-rounded to rounded, very fine to medium grains sizes composed by dark brown Kc kaolinites coated by iron oxides. Note the clear kaolinite cementing the interstitial space (bright color) (parallel polars). E) Sandstone from the semi-flint unit, characterized by a strongly kaolinitized fabric, but where sand grains can be distinguished (arrows) from the “matrix” of similar composition (SEM, back scatter). F) A detail of the interstitial space of a sandstone from the semi-flint unit, cemented by spherules of iron oxides. Note a few hairy crystals of halloysite (arrows) (SEM, secondary electrons). G, H) Details of tabular (G) and hairy (H) halloysite crystals that

occur cementing the kaolinitized sandstones of the semi-flint unit (SEM, secondary electrons).