Chapter 2
Azul County

Abstract This chapter is related to the geology, stratigraphy, petrology, mineralogy, and industrial applications of residual clay deposits of Azul County, Chillar Sector. Almost all of the outcrop rocks in the area of Azul correspond to the crystalline basement rocks (Complejo Buenos Aires), 2200–1800 Ma, belonging to the Trans Amazonic cycle (Teruggi and Kilmurray 1975, 1980; Dalla Salda et al. 1988, 1992). The mountain area is characterized by the presence of middle and high metamorphic grade (gneisses and migmatites) and of granitoid rocks, sometimes with variable degree of milonitization, produced by E–W-oriented shear zones. The residual clay deposits are weathering products of the crystalline basement rocks and are covered by siliciclastic sediments of the Balcarce Formation (oligomictic orthoconglomerates and quartzites). In the area of Azul, the clay deposits are located at the Estancia Santa María and La Verónica, in the vicinity of the national route Nº 3; 3 and 5 km to the SSE of the town of Chillar, respectively. Chillar clays are mineralogically classified as kaolinitic, and technologically, as refractory of high and medium quality, in coincidence with the high percentages of Al_3O_2 observed in the chemical analyses and the abundant content of kaolinite with subordinate dickite as predominant clay minerals in the saprock and in the saprolite as well.

Keywords Azul County · Chillar Sector · Geology · Stratigraphy · Mineralogy · Residual clay deposits · Technological properties

The County of Azul bounds to the North with Tapalqué and Las Flores counties, to the South with Benito Juárez County, to the East with Rauch and Tandil counties, and to the West with the Olavarría County. Almost all of the outcrop rocks in the area of Azul correspond to the crystalline basement rocks (Complejo Buenos Aires), 2200–1800 Ma, belonging to the Trans Amazonic cycle (Teruggi and Kilmurray 1975, 1980; Dalla Salda et al. 1988, 1992). The mountain area is characterized by the presence of middle and high metamorphic grade (gneisses and migmatites) and of granitoid rocks, sometimes with variable degree of milonitization, produced by E–W-oriented shear zones.

P.E. Zalba et al., *Gondwana Industrial Clays*,
Springer Earth System Sciences, DOI 10.1007/978-3-319-39457-2_2

In addition, conspicuous thick bands of cataclasites, mainly of granitic composition, are observed. In this set of rocks that make up the local metamorphic basement, there are regular size diabase dykes, often anphibolitized, presenting a predominantly NW direction (Dalla Salda 1981; Kilmurray et al. 1985; Etcheveste et al. 1997). Moreover, the Paleozoic sedimentary sequence (The Balcarce Formation, see Table 1.1) is restricted to the sector of Chillar (60 km S from Azul and 75 km to the west of Tandil. In this area the Balcarce Formation consists of variable thickness (between 8 and 20 m) of conglomerates and sandstones which overlie a weathered (saprolitized) crystalline basement rock. Oligomictic orthoconglomerates consist of very thick to thick tabular or lenticular strata, of light colors (gray, whitish) and sub-rounded clasts of chert composition (microcrystalline silica = chalcedony). The entire sequence, which is approximately 8 m thick in the area, culminates with quartzites, with abundant cross-bedding structures. The structure sinks regionally, with low-angle, towards the SE.

2.1 Chillar Sector

2.1.1 Residual Deposits: Characteristics, Mineralogical, and Chemical Composition

In the area of Azul, the clay deposits are located at the Estancia Santa María and La Verónica, in the vicinity of the national route Nº 3; 3 and 5 km to the SSE of the town of Chillar, respectively. These deposits are weathering products of the crystalline basement rocks (residual deposits) and are covered by siliciclastic sediments of the Balcarce Formation (oligomictic orthoconglomerates and quartzites).

La Verónica is the main site of exploitation where the extracted clay level represents a saprolitized zone (Fig. 2.1a) of the underlying crystalline basement rocks with a thickness varying between 1 and 4 m. Figure 2.1b represents a stratigraphic section in the La Verónica quarry, where the different areas of weathering of the basement rocks can be seen and, unconformably, over an erosive discordance, the sedimentary sequence of the Balcarce Formation lies.

According to petrographic analysis the base of the section corresponds to the weathering zone known as saprock since the excavation of the quarry does not reach the unaltered basement (bedrock). The saprock is recognized because, although the original mineral species remain as such, the rock already has a recognizable degree of alteration. The mineral species identified at this level are: plagioclase (oligoclase: An 17–22 %), some of them twinned and without alteration, and the most abundant, with no twins, have altered to kaolinite-dickite and, to a lesser extent, to illite-smectite, which appears as whitish dots (up to yellowish)

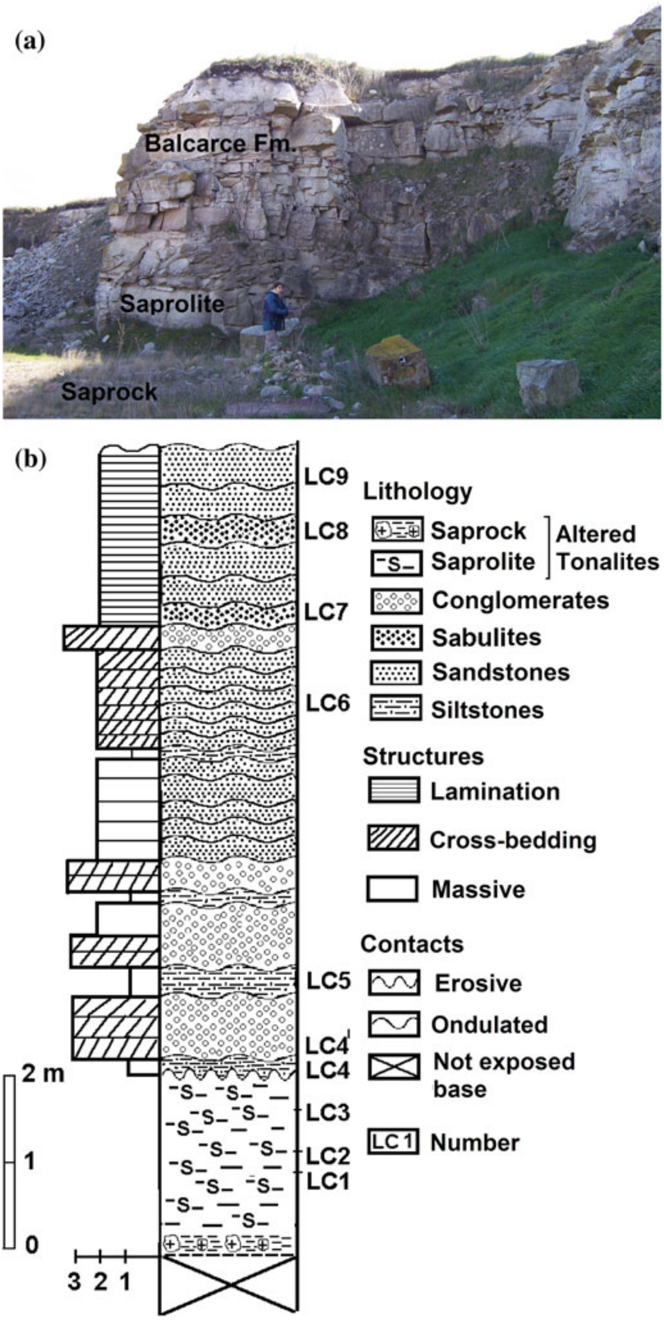

Fig. 2.1 **a** La Verónica quarry, Chillar. The clays mined correspond to the saprolite (altered basement). **b** Stratigraphic section carried out in the La Verónica quarry (Chillar), showing different alteration basement zones and the sedimentary sequence (Balcarce Formation). LC1/9: samples

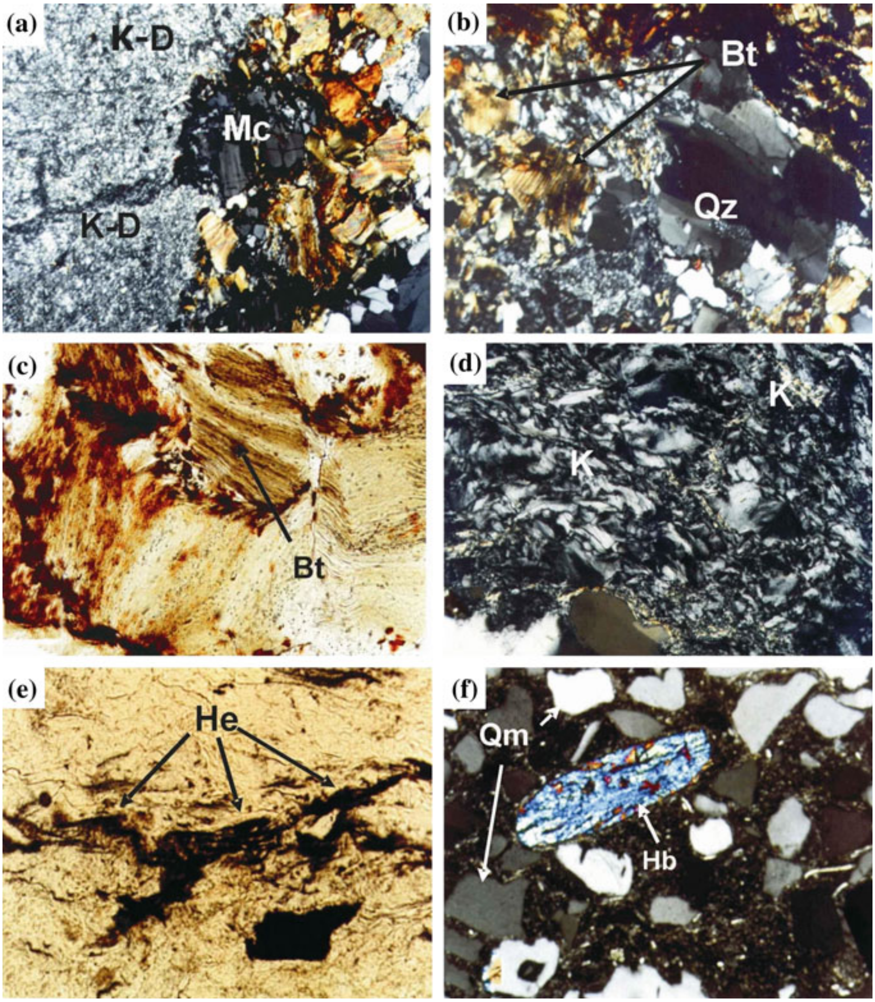

Fig. 2.2 Photomicrographs of La Verónica quarry, Chillar. Saprock: **a** Plagioclase altered to kaolinite-dickite (K-D) and scarce fresh microcline (Mc), (40x magnification). **b** Monocrystalline quartz with undulate extinction (Qz), Biotite (Bt) in the form of curved books of high birefringence (40x magnification). **c** Iron exhaust through open cleavages in biotite (Bt), (200x magnification). **d** Poorly defined kaolinite books (K), ghostly, (200x magnification). Saprolite: **e** Migration of hematite (He) into cracks and fissures, (200x magnification). Sedimentary level: **f** Monocrystalline quartz (Qm) and fresh hornblende (Hb), (100x magnification). Photomicrographs taken under cross polarized light (XPL)

within the plagioclase (Fig. 2.2a). Also the presence of scarce, fresh microcline was observed. Monocrystalline quartz (Fig. 2.2b) as well as abundant curved mica (biotite, Fig. 2.2c) of high birefringence, and which begins to alter to kaolinite, distinguished by its grayish colors are observed. The cleavages are opened and constitute the escape route of the iron contained in the mica structure. Zircon was identified as an accessory mineral.

Going upwards in the section, the level known as saprolite is reached. Here the original minerals (plagioclase, biotite) do not exist anymore. The alteration to clay minerals is complete. Kaolinite books, mostly, lose definition and become “ghostly” (Fig. 2.2d). The only relic of biotite is iron oxide (hematite), in some cases forming a laminar texture as vestige of the original mica texture, or either crystallizing into prismatic shapes (Fig. 2.2e). Hematite migrates to the cracks and fissures as well as the clays, which, in addition, surround quartz crystals (Fig. 2.2e). The altered basement rock (saprolite) is compact, with conchoidal fracture and reddish-gray to gray-green colored, occasionally reddish to the base due to the presence of iron oxides and hydroxides. The greenish gray coloration is due to the clay minerals. This is the exploited level of the quarry.

On the other hand, the clays of the first sedimentary levels, above the conglomerate of the Balcarce Formation (not exploited) show a completely different texture, with unaltered muscovites, monocrystalline quartz, fresh hornblende (Fig. 2.2f), and clays. The mineralogical composition of the clays in the La Verónica, analyzed by X-ray diffraction for this work (Table 2.1), is consistent with the interpretation of the petrographic analysis. It is essentially kaolinitic, in some sectors with high degree of purity, accompanied by scarce interstratified clay minerals: illite-smectite (IS), and very little smectite. The most common impurities are iron oxides and quartz, the latter found in varying proportions (12–56 %) in angular crystals, rarely exceeding 1 mm. Clays show a high degree of compaction. The presence of anatase denotes a high degree of weathering.

As for the Estancia Santa Maria (Table 2.2, samples SM) the base rock is of the same type and the same thickness as the one described at the La Verónica, although with some variations. Figure 2.3 shows a front of exploitation. The rock base corresponds to a level of weathered basement (saprock). Petrographic studies carried out for this study shows that black micas (biotites) are abundant while white micas (muscovites) are scarce.

Biotites are partially deferrized, with yellowish interference colors and varying degrees of alteration (Fig. 2.4a). Some crystals of biotite are flexured and oriented

Table 2.1 Mineralogical composition by X-ray diffraction, temperature and Pyrometric Cone Equivalent (PCE) of the studied samples in the La Verónica quarry. Samples LC 1-4 correspond to altered levels of basement. LC 5 is the first sedimentary clay level above the conglomerate of the Balcarce Formation

Sample	Quartz (%)	Kaolinite (%)	I/S (%)	Smectite (%)	Anatase (%)	Temperature (°C)	PCE
LC1	14	77	6	3	–	1680	31
LC2	12	80	5	3	–	1765	34
LC3	17	75	5	3	Traces	1700	31.5
LC4	24	70	4	2	Traces	1665	30
LC5	21	73	3	2	1	1680	31

Table 2.2 Mineralogical composition by X-ray diffraction, temperature and Pyrometric Cone Equivalent (PCE) of the studied samples in the Santa Maria quarry. Samples SM 0-2 correspond to residual deposits and SM3 corresponds to the sedimentary level of the Balcarce Formation

Sample	Quartz (%)	Kaolinite (%)	I/S (%)	Smectite (%)	Anatase (%)	Temperature (°C)	PCE
SM0	56	–	43	1	–	1621	26
SM1	39	56	4	1	–	1680	31
SM2	44	50	5	1	–	1680	31
SM3	38	54	5	1	2	1640	27

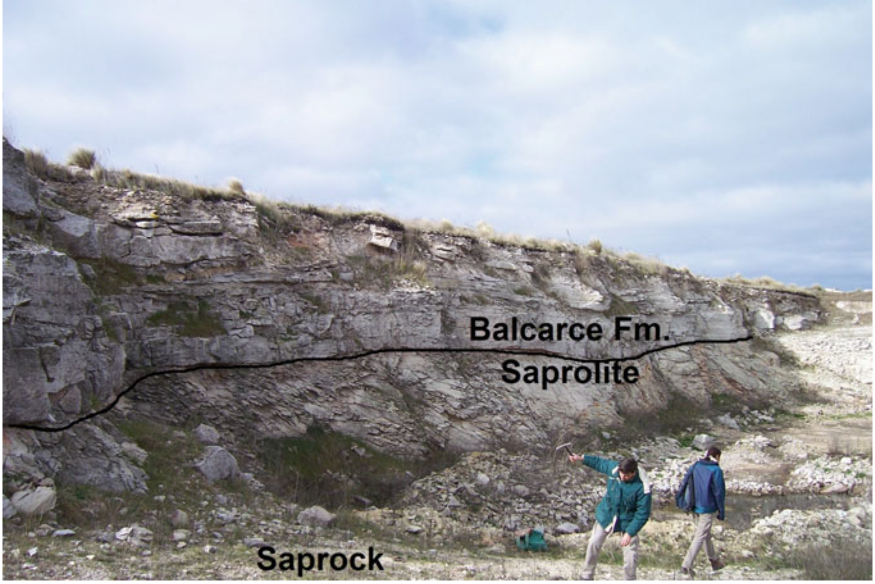

Fig. 2.3 Santa María quarry, Chillar. The clay level mined corresponds to the saprolite. The saprock forms the base of the quarry

around abundant monocrystalline quartz crystals. Ferric oxide (product of the deferrization of biotite) is located in its open cleavages and occupying intracrystalline and intercrystalline fractures and fissures. The plagioclase in this level of the saprock is very abundant, most of it is fresh and an incipient alteration to kaolinite-dickite is observed. The accessory minerals are crystals of zircon, in some cases, zoned. Following up on the profile the saprolite zone is reached where abundant plagioclase, with varying degrees of alteration to clay minerals such as kaolinite; dickite; illite-smectite (I/S) in the form of grayish to yellowish aggregates, mostly along the cleavages (Fig. 2.4b) are identified. Minor biotites are also deferrized and altered to clay minerals. Iron oxides are arranged on the lines of

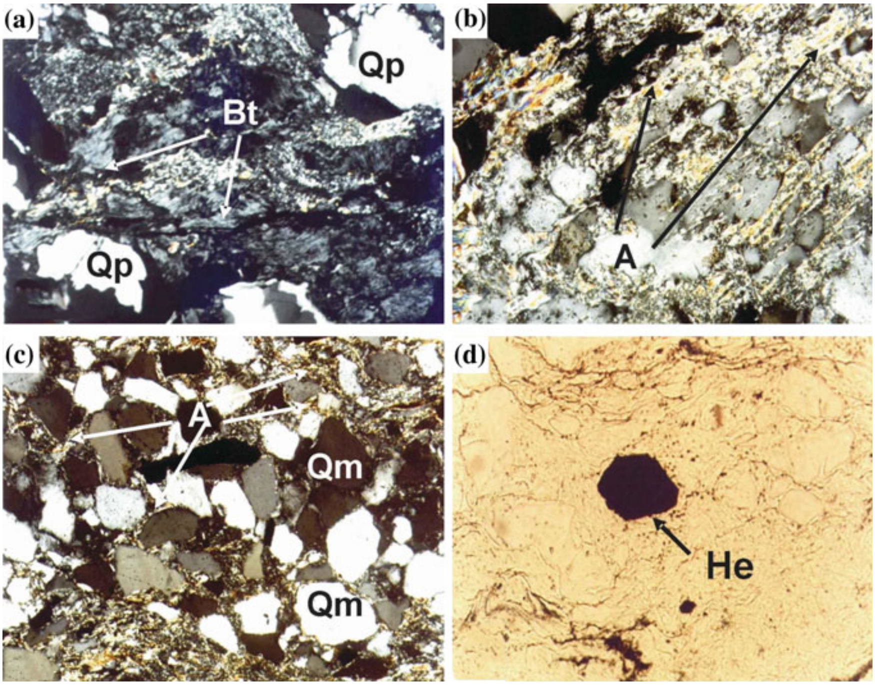

Fig. 2.4 Photomicrographs of Santa Maria quarry, Chillar. **a** Saprock: biotites partly deferrized and flexured (Bt); polycrystalline quartz (Qp), XPL, 200x magnification. **b** Saprolite: clay minerals (A) forming aggregates along the cleavage (K-D), XPL, 200x magnification. Sedimentary level: **c** laminates levels with alternating abundant sandy or abundant clay. Monocrystalline quartz crystals (Qm) surrounded by clay (A), XPL, 200x magnification. **d** Hematite hexagon (I) cross section. Photomicrograph taken under plane polarized light (PPL), 100x magnification

cleavage of biotite or forming irregular aggregates in pore spaces. Zircon is an accessory component. Clays migrate to fissures and surround abundantly various mineral species.

Continuing upward in the stratigraphic section, and above the conglomerate of the Balcarce Formation, sandy siltstone levels are recognized. A drastic change in the texture of the rock is detected. The deposits are laminated, with alternating abundant sandy or clayish levels. Monocrystalline quartz is very abundant and detrital clay coatings surround the clasts (Fig. 2.4c). Iron oxide crystallizes as irregular or prismatic hematite, and also it is observed in basal, hexagonal sections (Fig. 2.4d). Zircon crystals increase and are of rounded shapes. The presence of anatase in the sedimentary levels is a product of its remobilization from the crystalline rocks, formed in the upper part of the saprolite. These levels are not exploited.

The mineralogical composition by X-ray diffraction (XRD) of samples from the saprolite, studied in the Santa María quarry, is available in Table 2.2. Lateral variations in the mineralogical composition are appreciated taking into account the two mentioned deposits, especially at lower levels, corresponding to the saprock. Quartz is significantly more abundant at the Santa María, probably due to local variations of the original rock. The variation in the amount of quartz in LC5 and SM3 (sedimentary levels) is due to erosion and remobilization of the transported materials. On the basis of petrographic analyses, the basement rocks (bedrock) of both stratigraphic sections would correspond to biotitic tonalites.

Chemical analyses on samples from La Verónica and Santa María can be consulted in Table 2.3. Variable content of Al_2O_3 (15–31.6 %) is due to the destruction of plagioclase and muscovite and to the concentration of Al_2O_3 in the clay minerals of upper levels of the altered basement rocks. SiO_2 contents correspond to the addition of silica to the new formed clay minerals and the crystallization of quartz in cracks, except in SM3 and LC5 (sedimentary levels) which reflect erosion and transport processes.

The low Fe_2O_3 content (0.4–1.24 %) is explained because iron is the first element which solubilizes in a weathering profile. The low Na, Mg, and Ca contents and their variations, correspond, also, to the loss of these elements in a weathering profile, except in samples LC5 and SM3 (sedimentary levels) where their increase is due to the presence of unaltered muscovite transported to the basin. In terms of the variation in K content, this is consistent with the destruction of the muscovites as weathering progresses in the basement rocks. Its increase in LC5 and SM3 (sedimentary levels) is coherent with the presence of unaltered muscovite transported to

Table 2.3 Chemical composition of samples of La Verónica (LV) and Estancia Santa Maria (SM) quarries

Sample	LC1	LC2	LC3	LC4	LC5	SMO	SM1	SM2	SM3
Weigth %									
SiO_2	51.1	53.8	56.2	53.3	54.2	76.1	72.6	71.2	61.3
Al_2O_3	31.9	30.0	28.9	31.6	30.0	15.1	18.85	19.55	23.0
Fe_2O_3	1.24	1.00	1.07	1.12	0.70	0.43	0.44	0.43	0.69
CaO	0.21	0.30	0.16	0.17	0.41	0.21	0.09	0.30	0.61
MgO	0.20	0.24	0.14	0.15	0.26	0.17	0.14	0.14	0.44
Na_2O	0.02	0.01	0.01	0.01	0.06	0.02	<0.01	0.01	0.03
K_2O	0.83	0.80	0.41	0.38	0.63	3.89	0.85	0.67	1.34
Cr_2O_3	0.01	0.02	0.03	0.01	0.02	<0.01	<0.01	0.01	0.03
TiO_2	1.79	1.34	1.19	1.08	1.25	0.37	0.39	0.36	2.26
MnO	0.01	0.01	<0.01	0.01	0.01	0.05	<0.01	0.01	<0.01
P_2O_5	<0.01	<0.01	0.07	< 0.01	0.01	0.06	<0.01	0.02	0.09
SrO	0.01	<0.01	0.01	<0.01	0.01	0.01	<0.01	<0.01	0.01
BaO	0.02	0.02	0.01	0.02	0.02	0.03	0.01	0.05	0.05
H_2O-	0.85	1.16	0.70	1.05	0.98	0.70	0.39	0.44	1.23
H_2O+	11.75	11.35	11.05	12.5	10.9	2.40	6.55	6.97	7.82
LOI	12.45	12.25	11.35	12.6	12.4	3.24	6.88	7.32	9.47
Total	99.8	99.8	99.6	100.5	100	99.7	100	100	99.3

the basin. The TiO_2 increase in sedimentary levels (LC5 and SM3) is due to its remobilization, originally contained in the muscovite, and to the formation of anatase, and, also, to the transport of fresh muscovite to the basin.

2.1.2 *Scanning Electron Microscopy of Clays of La Verónica*

Texture and mineralogical composition of the saprock from the La Verónica is exemplified by SEM. Incipient (very rarely observed) pseudo hexagonal kaolinite crystals formed from feldspar (plagioclase) are shown. The crystals are grouped into "accordions" or "books", typical of neoformed kaolinite. Also, in the right half corner of the picture, a crystal of goethite (G), with serrated edges (Fig. 2.5a) is observed. Figure 2.5b also belongs to the saprock and shows very thin goethite

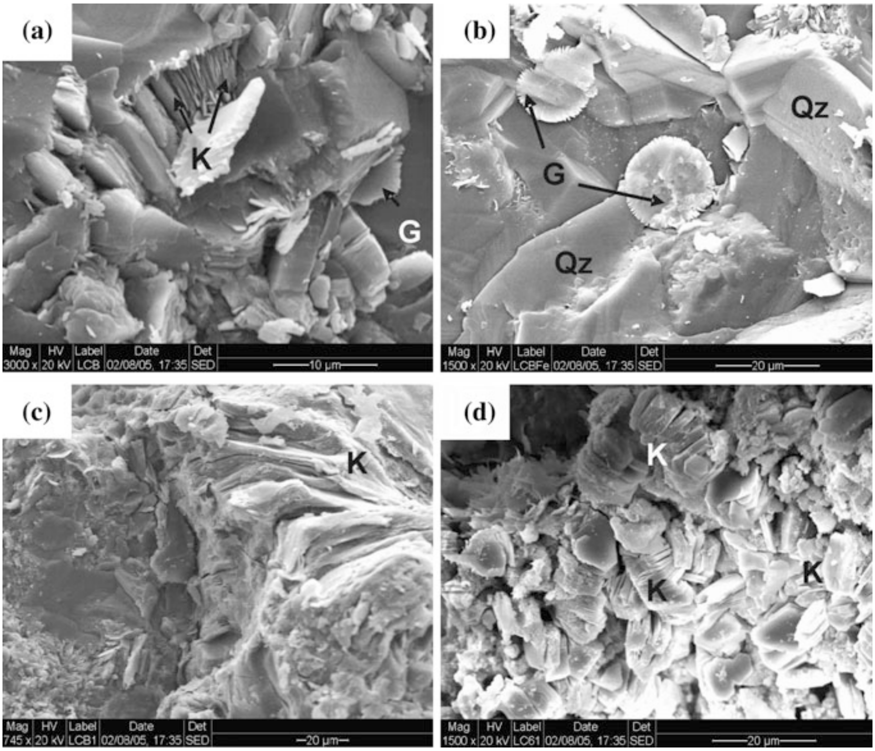

Fig. 2.5 Scanning electron micrographs. La Verónica quarry. Saprock: **a** Kaolinite crystals growing from a plagioclase. **b** Goethite crystals growing over quartz crystals. Saprolite: **c** Partly deferrized micas through open cleavages and transformed into kaolinite. Sedimentary level: **d** Accordions of pseudo hexagonal diagenetic kaolinite. The bar indicates the scale of the microphotographs

crystals growing over quartz crystals, indicating the paragenetic sequence. In the saprolite, packages of ex-micas, partly deferrized, through open cleavages, and transformed into kaolinite can be seen in Fig. 2.5c. On the other hand, Fig. 2.5d exhibits the diagenetic growth of regular, pseudohexagonal kaolinite "accordions", as well as of illite-smectite (upper left sector of the image) of filamentous forms, in the pores of sandstone (quartzites), in the sedimentary deposits of the Balcarce Formation, overlying unconformably the saprolite.

2.1.3 Technological Properties of Residual Clays of La Verónica and Santa Maria

On the basis of mineralogical and physico-chemical analyses carried out by the authors for this work, and those taken from the geological literature (Schalamuk et al. 1992), it can be concluded that the clays of the saprolite in the area of Chillar have scarce variations. The plasticity index is between 3 and 5, the bulk density is between 2.05 and 2.1, the apparent porosity varies between 18.3 and 23.2 % and the Pyrometric Cone Equivalent (PCE) is between 26 and 34. The refractoriness of a material is inversely proportional to the alkalis content, and values of refractoriness are presented in Table 2.4. The PCE analysis for refractory materials indicates the temperature at which the material becomes soft by the action of heat. The essay was carried out according to the method detailed in the standard IRAM 12,507. The color of the piece after burning is ivory white, which will result in a clear ceramic as a final product.

Chillar clays are classified as refractory with high (PCE 31–34) and medium (PCE 26–27) quality, in coincidence with the high percentages of Al_3O_2 observed in the chemical analyses and the abundant content of kaolinite with subordinate dickite as predominant clay minerals in the saprock and in the saprolite as well.

Table 2.4 Pyrometric Cone Equivalent (PCE) and temperature of the analyzed samples of La Verónica and Santa Maria quarries

Sample	Temperature (ºC)	P.C.E.
LC1	1680	31
LC2	1765	34
LC3	1700	31.5
LC4	1665	30
LC5	1680	31
SMO	1621	26
SM1	1680	31
SM2	1680	31
SM3	1640	27

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http://www.springer.com/978-3-319-39455-8

Gondwana Industrial Clays
Tandilia System, Argentina-Geology and Applications
Zalba, P.E.; Morosi, M.E.; Conconi, M.S.
2016, IX, 168 p. 74 illus., 43 illus. in color., Hardcover
ISBN: 978-3-319-39455-8