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Halloysite in Argentinian deposits: origin and textural constraints

F. CRAVERO[1,2,*], P. J. MAIZA[1,2] AND S. A. MARFIL[1,3]

[1] *Department of Geology, INGEOSUR. Universidad Nacional del Sur. San Juan 670. 8000 Bahía Blanca. Argentina,* [2] *Researcher at CONICET. Argentina, and* [3] *Researcher at CIC of the Province of Buenos Aires. Argentina*

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ABSTRACT: In Argentina, the only halloysite deposits found so far are located in the southwest of the province of Rio Negro. The areas are named Mamil Choique and Buitrera, separated by 50 km in a W–E direction. The deposits are located in pyroclastic rocks, rhyolitic tuffs and ignimbrites.

The aim of this paper is to determine the origin of the alteration, any relationship between the processes in Mamil Choique and Buitrera, and the factors which controlled the halloysite formation. The work was based on field work, mineralogical and geochemical studies, form and distribution of the alteration. Fresh as well as altered rocks were collected. The first were studied by petrographic and chemical methods. In altered samples, the clay mineralogy was determined by XRD and textures by SEM and TEM. Chemical analyses on fresh and altered samples were used to characterize the alteration process and the rock composition.

It was concluded that halloysite has been formed by weathering in a time range from Middle Eocene to Middle Oligocene and extended along 50 km in a W-E direction, independent of the source rock. Particle morphology depends on the original texture of the rock. Spheroidal halloysite is related to rocks with low porosity and tubular particles are related to rocks with open spaces.

KEYWORDS: halloysite, kaolin, Patagonia, Argentina.

Halloysites are defined by the presence or evidence of past occurrence of interlayer water in a mineral with a kaolin-type structure (Churchman & Carr, 1975). Halloysites and kaolinites have identical chemical compositions, being composed of aluminosilicate layers comprising $Al_2Si_2O_5(OH)_4$, except that a halloysite may have as many as two molecules of H_2O, as interlayer water, for each $Al_2Si_2O_5(OH)_4$ (Churchman *et al.*, 2010). The interlayer water in halloysite-(10 Å) is an essential feature distinguishing halloysite from the other polymorphs of the kaolin group, but it irreversibly dehydrates to a 7 Å structure. The content of additional water in the interlayers has a decisive influence upon its crystal morphology, which is generally curled rather than platy like kaolinite.

Halloysite results from weathering, pedogenesis or hydrothermal alteration of ultramafic rocks, volcanic glass and pumices. The occurrence of halloysite is favoured by humid or water-saturated environments and by high silica activity when formed directly from the dissolution of primary minerals (volcanic glass or crystalline minerals) (Joussein *et al.*, 2005). Churchman *et al.* (2010) studied the occurrence of halloysite and/or kaolinite in clay-rich, vein-like zones in saprolites from Hong Kong and concluded that the persistent presence of water is necessary for the formation of halloysite. Under otherwise similar environmental and chemical conditions, kaolinite is formed rather than halloysite where drying occurs; and either

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* E-mail: fcravero@uns.edu.ar
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halloysite or kaolinite form in larger particles when soluble impurities are absent in the solutions for their neogenesis.

Particle morphology has been related to crystallization conditions and geological occurrence. The work of various authors shows that spheroidal halloysite is common in weathered ashes and pumices whereas tubular halloysite is commonly derived from crystalline minerals (Joussein *et al*., 2005). Adamo *et al.* (2001) found that the difference in morphology is related to the original texture of the rock. Papoulis *et al.* (2004) found four different stages in the kaolinization process of the felsic facies of an amphibolitic gneiss in Greece. Kaolinite predominates at the surface of the highly weathered gneiss, platy and tubular halloysite predominate at deeper levels and spheroidal halloysite is found at the base of the profile near the fresh rock. They consider that the chemical composition of the ambient solutions is the main factor dictating the nature of the solid phase formed.

Halloysite deposits are not frequent in the geological record. The main deposits are located in New Zealand, Japan, China and United States. The most extensive halloysite deposits are in New Zealand. In the North Island (Maungapaperua), deposits of halloysite have been formed by hydrothermal alteration of rhyolitic rocks on which residual weathering has been superimposed (Murray *et al*., 1977), whereas Harvey (1997) found that halloysite was formed by weathering in some rhyolitic domes, and kaolinite was the main phase in the hydrothermal zone. In Japan, the main deposits are at Imura and Iki; halloysite was formed after the alteration of vitreous rocks by surficial hydrothermal solutions (Sato, 1969). In China, a small deposit has been formed by hydrothermal alteration of volcanic rocks structurally controlled and related to limestones. Turkish deposits and those at the Dragon Mine in the USA are similar to those in China in both genesis and size (Wilson, 2004).

Halloysite-bearing pyroclastic deposits are present in the Roccamonfina volcanic area of southern Italy (Adamo *et al*., 2001). They suggested that the process of formation probably involves: (a) dispersion and deposition of erupted pyroclastic materials all over the volcanic area; (b) water erosion and accumulation in the valleys of the volcanic products; and (c) *in situ* attack by water containing dissolved carbon dioxide. Parham (1969) proposed that halloysites formed as weathering products in humid tropical conditions would act as seeds for further kaolinite growth as long as the humid conditions remain.

In Argentina, halloysite as the main alteration product has been mentioned in few areas. Rossi (1969; in Domínguez & Maiza, 1984) pointed out that halloysite, kaolinite and sericite, along with cristobalite and sanidine, are present in La Buitrera I and II of Río Negro Province and that the same type of mineralization could be found in the same province in the Mamil Choique area. Cravero *et al*. (2009) described the halloysite deposits of Mamil Choique as formed by weathering of the ignimbritic rhyolites of the Huitrera Formation (Eocene). Halloysite with minor kaolinite makes up 80% of the altered rocks. The depth of the alteration is variable from a couple of metres up to 10 m, but with no vertical zonation. Spheroidal halloysite predominate in these deposits.

Mamil Choique and La Buitrera are 50 km apart in a W–E direction in a similar geological environment. In between, there are several localities where the rocks are also altered to halloysite. In these areas, tubes predominate over spheroidal halloysites. The extension of the alteration, the high ratio halloysite/rock, not common in this type of deposit, the formation of halloysite rather than kaolinite in different rocks at the same time and with different morphologies, make these areas of interest to contribute in our understanding of the conditions of formation of halloysite.

A comprehensive study of the source rocks, alteration and particle morphology in Mamil Choique and Buitrera has been carried out in order to determine the factors which controlled the halloysite formation.

MATERIALS AND METHODS

During field work, fresh and altered rocks were collected from each area. Fresh samples were study by petrographic and chemical methods. In altered samples, the clay mineralogy was determined by X-ray diffraction (XRD) and textures by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Chemical analyses on fresh and altered samples were used to characterize the alteration process and the rock composition.

Petrographic determinations were made with an Olympus B2-UMA trinocular petrographic microscope with a built-in Sony 151A video camera, a high-resolution monitor and Image-Pro Plus image processing software. Halloysite was determined by XRD, using a Rigaku D-Max III, with Cu-$K\alpha$ radiation and a graphite monochromator operated at 35 kV and 15 mA. XRD patterns were recorded from 2° to 60° 2θ. The distinction between halloysite and kaolinite was made by formamide intercalation (Churchman *et al.*, 1984) which, in less than an hour, produces an expansion from 7 Å to 10 Å in halloysite, whereas in kaolinite it takes about four hours. The ratio between halloysite and kaolinite was determined using the formula $I_{10}/(I_7 + I_{10})$ after formamide intercalation. Textural studies on altered samples were made with SEM (EVO 40XVP Leo) and TEM (JEOL JSM-100 CX II). More than 30 samples were analysed, about 20 from Mamil Choique and 10 from Buitrera, in order to study the different halloysite morphologies.

Chemical analyses for major, minor and trace elements were carried out by inductively-coupled plasma mass-spectrometry (ICP).

GEOLOGICAL SETTING

The studies were carried out on the Mamil Choique and Buitrera deposits separated 50 km in a W–E direction. They are located in the southwest of Rio Negro Province, approximately 80 km to the south of the town of Ingeniero Jacobacci (Fig. 1).

The deposits in both areas are located in pyroclastic rocks, rhyolitic tuffs and ignimbrites. Cravero *et al.* (2009) determined that the Mamil Choique deposits were formed on rhyolitic to dacitic pyroclastic rocks that belong to the Huitrera Formation of Eocene age. These rocks belong to the Eastern Belt of the Volcanic Andean Patagonic Province of Palaeocene–Eocene age (also known as Serie Andesítica) (Pankhurst *et al.*, 2006). In this area, several quarries (Rosas, San Martín, Pama, Belgrano and Santiago) have been opened to mine the halloysite although the main mineral sought is kaolinite and it is commercialized as such. They comprise small basins in between highs of fresh unwelded ignimbritic rocks. The largest mined area (Belgrano) is about 50 m^2 by 20 m deep. The vertical limit of the exploitation is marked when a light blue welded ignimbrite is reached. The western deposits lie over porphyiric granites of the Mamil Choique Formation (Carboniferous) and are covered by Pliocene basalts of the Campana Formation.

According to the geological map (Servicio Geológico Minero, 2000), Fig. 1, the Buitrera deposits have been formed on pyroclastic rocks of

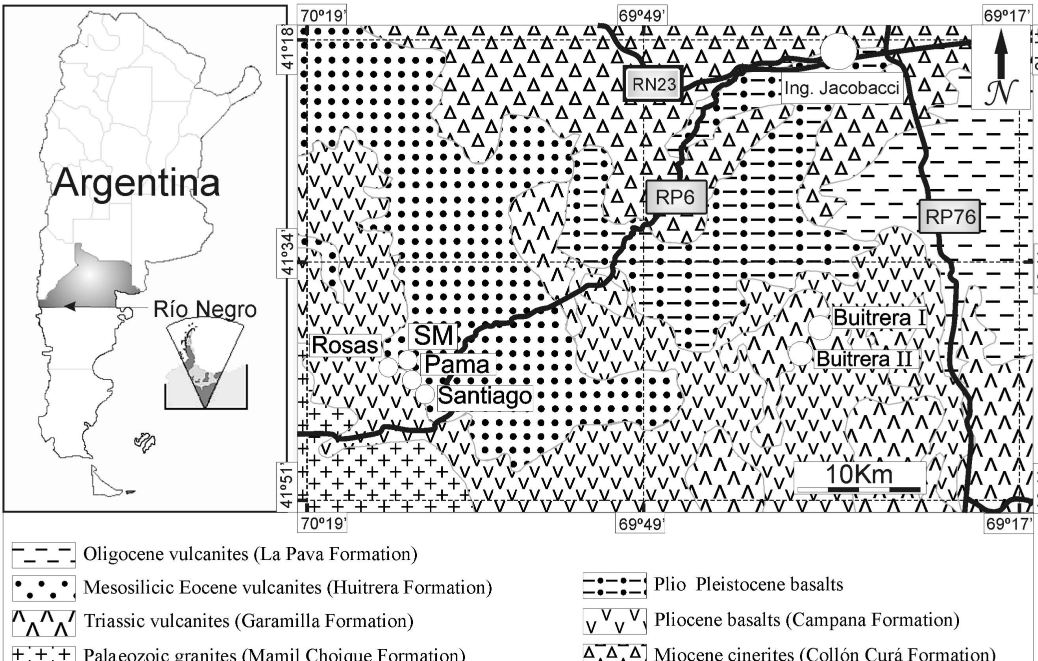

FIG. 1. Geological setting, after Servicio Geologico Minero (2000), and location of the study area.

the Garamilla Formation of Triassic age. This formation is composed of rhyolites, ignimbrites, rhyolitic tuffs and vitrophyres. The deposits are small, about 1000 m^3, and were formed by the alteration of rhyolitic tuffs (Rossi, 1969; in Domínguez & Maiza 1984).

In between the deposits there are outcrops of andesitic lavas and tuffs of the Traquetren Formation of Upper Jurassic age (Lizuain & Silva Nieto, 1996).

RESULTS – PETROGRAPHY AND MINERALOGY

Country rock

Mamil Choique area. Two different types of rocks have been found.

(1) A light blue strongly welded ignimbrite with disc shaped fiammes. Under the microscope, the glass has been devitrified to spherulites; fiammes are filled with vapour phase minerals such as tridymite (Fig. 2a). Crystaloclasts are scarce, represented mainly by sanidine. This rock was found at the bottom of a drill hole in the Pama deposit and in Rosas, where the exploitation stopped when it was found at depth. It is classified as a rhyolitic to dacitic ignimbrite.

(2) A red-brownish, poorly welded ignimbrite Fig. 2b. Under the microscope it is composed of crystaloclasts of plagioclase, scarce biotite and lithoclasts in a glassy matrix where the ash shards are welded but the rock can be still recognized. The glass has been devitrified to a spherulitic texture (Fig. 2c). It is classified as a trachyte.

Buitrera area. The rock has been extensively devitrified to thin tabular feldspars and cristobalite. The original texture has been totally obliterated (Fig. 2d).

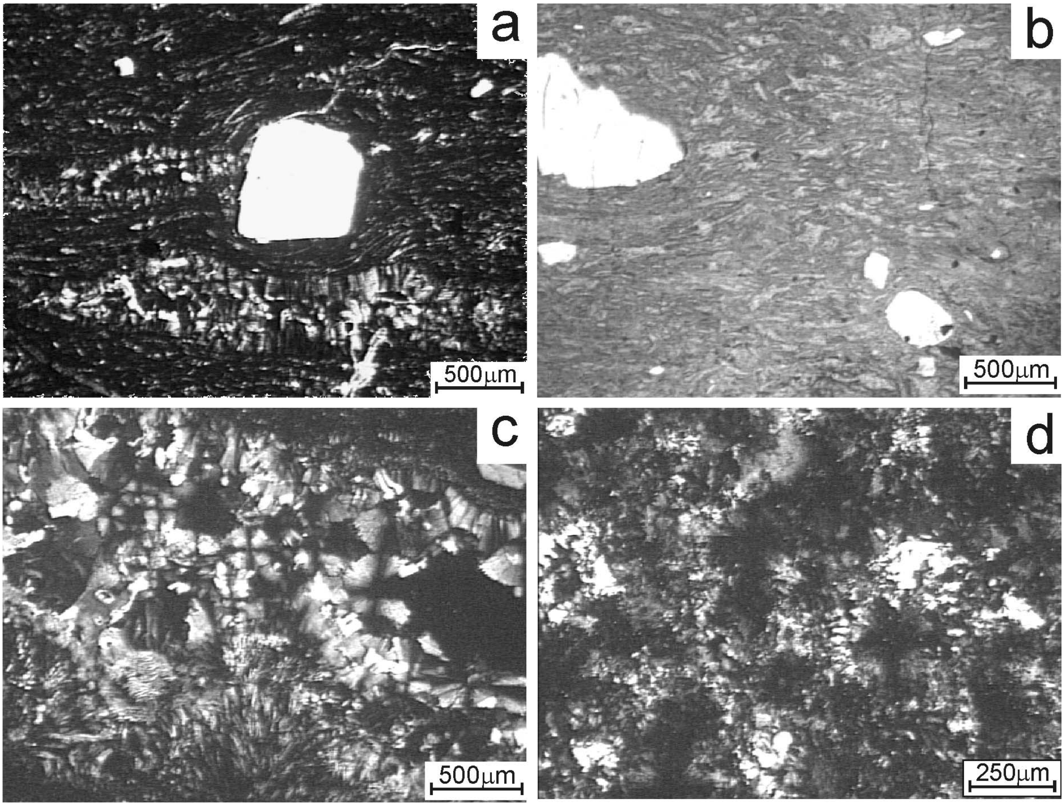

FIG. 2. Country rock. (a, b and c) Mamil Choique area. (a) Blue strongly welded ignimbrite with disc-shaped fiammes. (b) Red brownish poorly welded ignimbrite. (c) Traquite. The glass has been devitrified to a spherulitic texture. (d) Buitrera Area. The rock has been devitrified to thin tabular feldspar and cristobalite.

Alteration

Under the petrographic microscope the alteration is seen as an almost isotropic, very fine grained mass. In all the deposits halloysite is the main alteration product with minor kaolinite. Cristobalite, tridimite, and orthoclase are also present in XRD traces but are considered as glass devitrification products.

The Mamil Choique deposits are extensively altered with a halloysite/kaolinite ratio greater than 75/25, mostly 100% (Cravero *et al.*, 2009). In Buitrera, the alteration is weaker and only halloyiste has been found

SEM and TEM analyses show that in 80% of the samples taken in Mamil Choique, spheroidal halloysite is the predominant form, along with 0.5 × 0.2 μm tubes. Spheres form a packed texture whereas tubes are found forming a more open texture (Fig. 3a, b, c and d). In all the samples analysed from Buitrera, tubes predominate over spheres (Fig. 3e and f). Tubes grow from the surface pointing towards open spaces (Fig. 3d). Fig. 3e shows dissolution of the glass and growth of halloysite.

RESULTS – CHEMISTRY

Country Rock

In volcanic rocks it is very difficult to recognize the composition of groundmass and glass by optical methods. This makes it more difficult to establish a qualitative comparison between lithological groups especially when dealing with ignimbrites and pyroclastic facies. On the other hand, when the rocks are silicified, classification from chemical analysis is not accurate. Therefore, to identify the rocks both methods are used.

From chemical analyses (Table 1), all the rocks can be classified as rhyolitic to dacitic in composition (Fig. 4) of a peraluminous type (Fig. 5) with high calc-alkaline affinity that is typical of low-grade ignimbrites of orogenic environments (Llambías, 2003) (Fig. 6). These rocks are classified as trachytes under the microscope but in fact are rhyolites, because the silica content is in the glassy groundmass. Sample R2 is altered, the evidence being the slightly high LOI (about 10%). Because of this it falls in the dacitic field and is outside the field of the other samples in Figs 5 and 6.

In spite of the rock compositions, differences in the concentration of some minor and trace elements allow identification of two different groups; Group I with a strong Eu anomaly, and low Ba+Sr and Ti contents, and Group II with normal Eu anomaly, and high Ba+Sr and Ti contents (Figs 7, 8a and b). To Group I belong all the ignimbrite rocks with a high degree of welding and very small amounts of crystaloclasts. In Group II the ignimbrites show poor welding and the common presence of feldspars and plagioclases as crystaloclasts. Group I rocks are present in Mamil Choique as well as in Buitrera but Group II is only found in Mamil Choique.

TABLE 1. Chemical analysis of major elements (wt.%) of country rocks from the Mamil Choique and Buitrera areas.

	Group I				Group II				
	Pama		Rosas	Buitrera	Pama		Rosas		San Martin
	P1	P2	R1	B1	P3	P4	R2	R3	SM1
SiO_2	75.65	74.89	76.44	75.17	68.25	66.75	58.57	66.71	63.97
Al_2O_3	12.84	12.40	12.61	12.67	15.32	15.22	18.12	15.53	15.79
$Fe_2O_{3(T)}$	1.16	2.64	1.4	1.47	3.55	4.16	2.91	3.71	5.11
MnO	0.009	0.012	0.008	0.02	0.048	0.064	0.175	0.035	0.04
MgO	0.06	0.08	0.16	0.15	0.41	0.47	1.01	0.33	0.74
CaO	0.20	0.13	0.15	0.24	1.92	2.04	2.54	2.22	2.2
Na_2O	3.84	3.88	3.75	3.72	4.42	4.12	3.04	4.11	3.98
K_2O	4.90	4.89	4.87	4.21	4.02	3.84	2.44	3.88	4.03
TiO_2	0.144	0.121	0.12	0.121	0.576	0.626	0.723	0.63	0.706
P_2O_5	0.10	0.04	0.01	0.09	0.06	0.04	0.05	0.11	0.21
LOI	1.26	1.19	1.41	1.83	1.95	2.35	10.12	2.1	3.06
Total	100.16	100.26	100.9	99.69	100.51	99.68	99.68	99.37	99.84

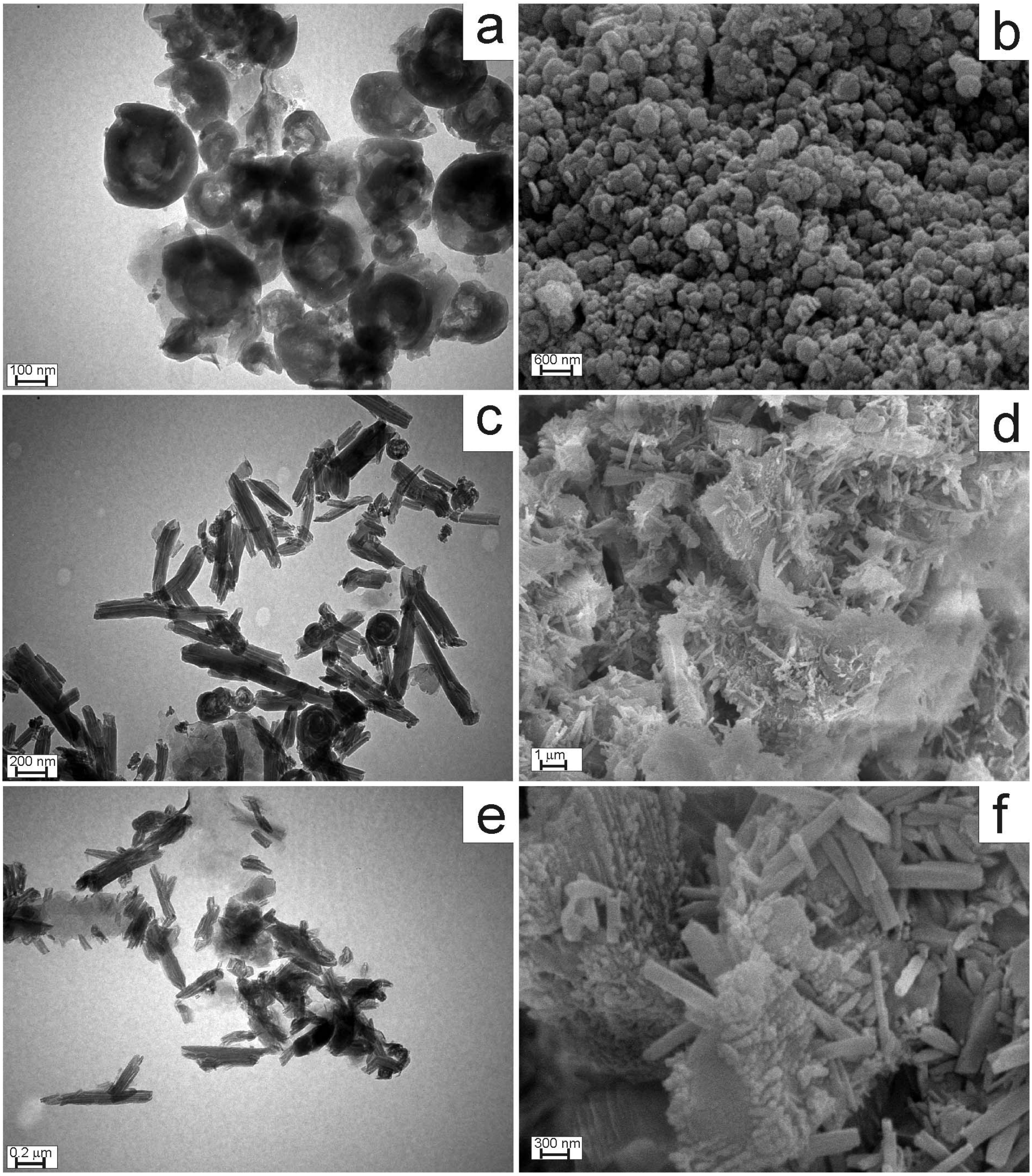

FIG. 3. SEM and TEM images of the alteration products. (a, b, c and d) Mamil Choique area. Spheroidal halloysite is the predominant form, along with 0.5×0.2 µm tubes. Spheres form a packed texture (b), whereas tubes are found forming a more open texture (d and e). (e and f) Buitrera area. Tubes predominate over spheres.

Because the alteration has obliterated the original texture, the chemical compositions of the altered samples are compared with those of the two groups of rocks already defined in order to identify their parent rock area. Figure 9a and b shows that in Mamil Choique, altered samples from different quarries show similar chemical behaviour to Group II rocks. On the contrary, altered samples from Buitrera are similar to Group I rocks.

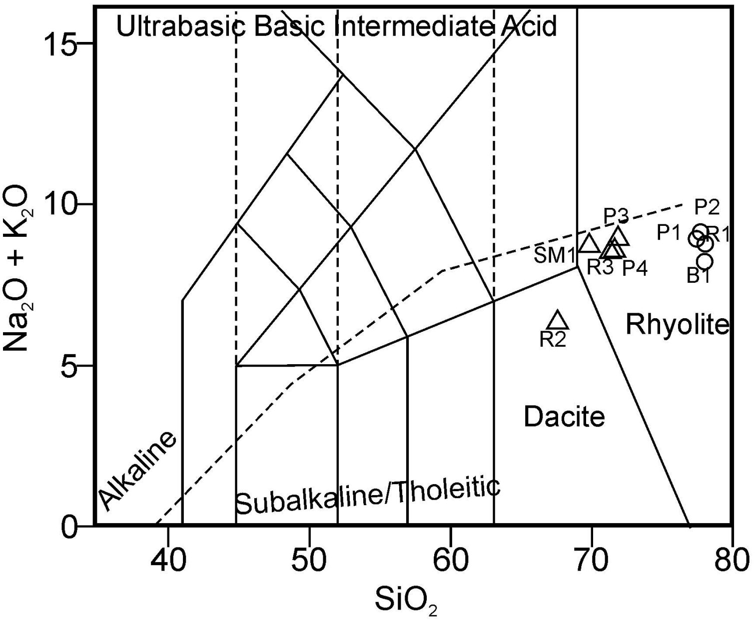

FIG. 4. TAS diagram (Le Bas *et al.*, 1986). All the rocks can be classified as rhyolitic to dacitic in composition.

Alteration

The chemical compositions of the altered rocks from the Mamil Choique and Buitrera areas are shown in Tables 2 and 3. Halloysite is the main alteration product and kaolinite is present in a few samples only from the Mamil Choique area. Alteration is characterized by the loss of SiO_2,

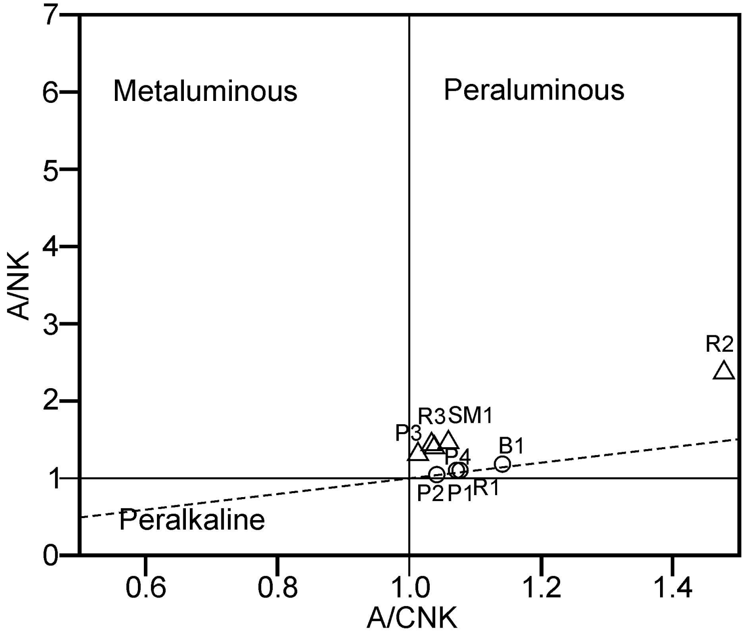

FIG. 5. A/CNK *vs*. A/NK plot (Shand, 1943). The country rocks are a peraluminous type.

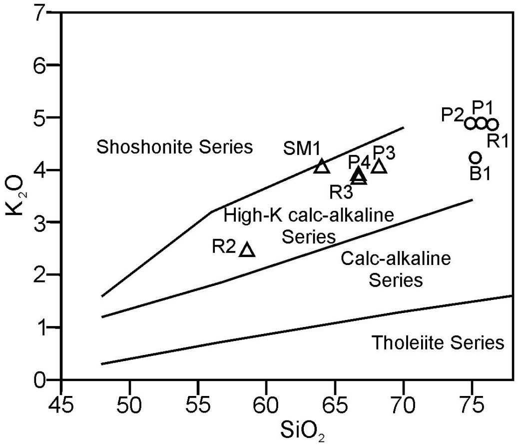

FIG. 6. SiO_2 *vs.* K_2O diagram (Peccerillo & Taylor, 1976). The rocks have a high calc-alkaline affinity.

Na_2O, K_2O, Ba, Sr and Rb, while Al_2O_3 and TiO_2 remain immobile. In the Mamil Choique area, depletion in *LREE* and enrichment of *HREE* have been observed in some samples (Fig. 10).

The strong Eu anomaly in Group I rocks implies that these rocks are from a felsic melt where feldspar had been removed, or from the partial melting of a rock where the feldspar was retained at the source (Rollinson, 1993). Group II rocks do not show this strong anomaly and are composed of crystaloclasts of feldspar and plagioclase. When these rocks undergo an alteration process, Eu is not mobile, so the altered rocks must show the same pattern as the fresh rocks. This characteristic permits recognition that in the Mamil Choique area, Group II rocks are those which alter, whereas in Buitrera they are Group I rocks.

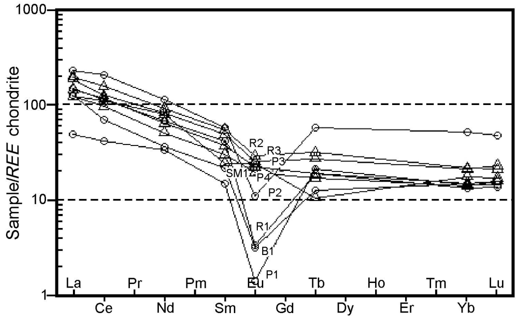

FIG. 7. Spider plot utilizing *REE* chondrite data (Boynton, 1984). Two different groups can be seen: Group I with a strong Eu anomaly and Group II with normal Eu anomaly.

DISCUSSION

According to the geological map, the alteration has proceeded in rocks that are of different ages but of the same composition. On the contrary, the chemical compositions of the rocks studied are similar and show an orogenic origin, which is coherent with the tectonic environment of the Huitrera Formation (Rapela *et al.*, 1984). These authors established that this Palaeogene volcanism is part of a subduction complex on the continental margin of the South American plate. It can be considered that the rocks which outcrop in Buitrera belong to the Huitrera Formation and not to the

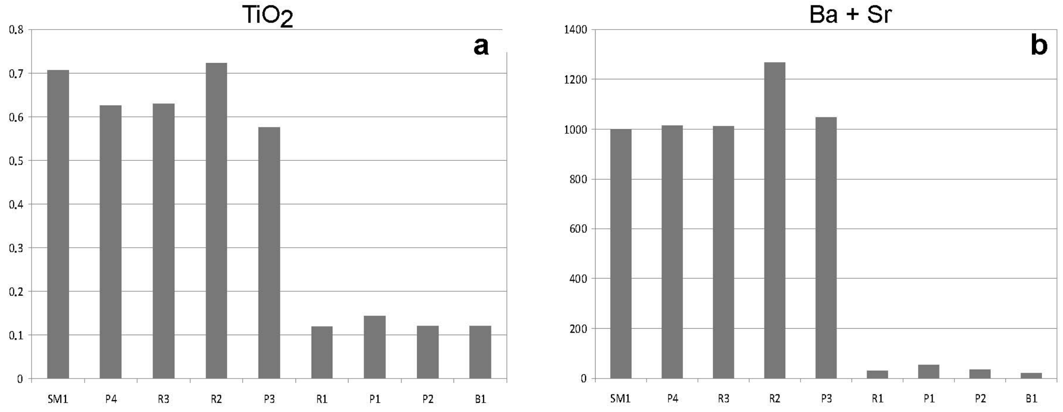

FIG. 8. (a) TiO_2 for samples. (b) Ba + Sr for samples. Group I shows low Ba+Sr and Ti contents and Group II high Ba+Sr and Ti contents.

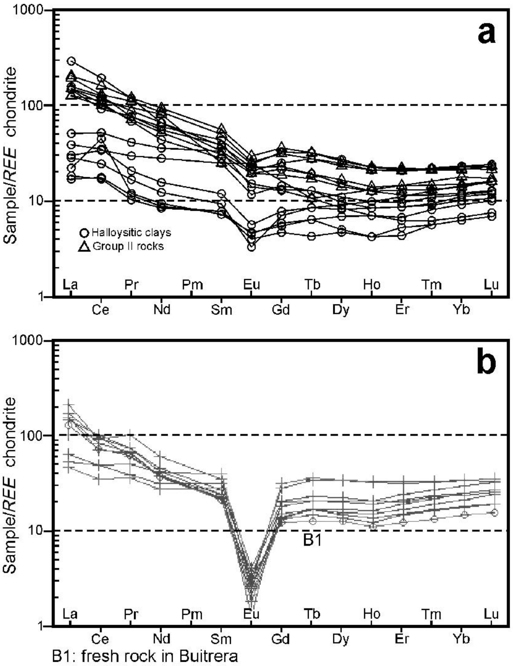

FIG. 9. Spider plot utilizing *REE* chondrite data (Boynton, 1984). (a) Altered samples from Mamil Choique. (b) Buitrera altered samples.

Garamillo Formation. From the geological map it is evident that small outcrops of the Huitrera Formation have been mapped in nearby areas.

According to Rapela *et al.* (1984), the morphology of the area was a large field of ignimbrite calderas and vitrophyric domes associated with shallow basins that collected the pyroclastic material and where, in the later stages, a fissural eruption of basic lavas occurred. The alteration process seems to be related to weathering conditions, where leaching of the mobile elements has been the main mechanism. There is no evidence of the addition of new elements or of high temperatures that could indicate hydrothermal activity. The lateral extension of the process is also in agreement with a weathering origin. Between these two areas, other small deposits of halloysite are found (Cravero, oral communication).

To form halloysite, a high water/rock ratio is needed. There is no evidence of vertical zonation that could indicate a downward alteration. It is probable that waters circulating towards small basins filled with these rocks came into contact with them for long periods of time, and halloysite

TABLE 2. Chemical analysis of major elements (wt.%) in altered samples from the Mamil Choique area.

	Pama						Santiago								Rosas	S.M
	HP1	HP2	HP3	HP4	HP5	HP6	HS1	HS2	HS3	HS4	HS5	HS6	HS7	HS8	HR1	HSM1
SiO_2	43.57	42.61	40.85	43.61	48.68	47.77	47.72	40.02	40.42	41.83	39.5	41.62	38.56	38.63	45.98	44.04
Al_2O_3	29.41	28.36	28.65	34.24	32.08	31.70	27.25	30.13	28.8	28.97	28.94	29.93	29.03	28.87	27.37	32.47
Fe_2O_3	1.36	1.21	0.67	0.79	0.50	1.72	0.81	0.67	0.8	1.1	0.57	0.81	0.69	0.74	0.9	0.74
MnO	0.009	0.007	0.006	0.009	0.005	0.007	0.021	0.006	0.011	0.007	0.007	0.01	0.008	0.006	0.006	0.007
MgO	0.24	0.12	0.12	0.11	0.22	0.24	0.25	0.17	0.21	0.27	0.21	0.25	0.18	0.19	1.43	0.15
CaO	0.3	0.19	0.2	0.20	0.26	0.44	0.25	0.24	0.26	0.34	0.24	0.33	0.26	0.25	0.59	0.19
Na_2O	0.12	0.08	0.17	0.12	0.25	0.20	0.18	0.17	0.24	0.24	0.3	0.17	0.24	0.23	0.17	0.27
K_2O	0.24	0.08	0.24	0.08	0.18	0.20	0.16	0.06	0.08	0.11	0.17	0.08	0.09	0.08	0.1	0.08
TiO_2	0.927	1.67	1.486	1.411	1.191	1.313	1.967	1.172	1.423	1.764	1.32	1.574	1.438	1.783	0.429	1.461
P_2O_5	0.06	0.04	0.02	0.05	0.03	0.05	< 0.01	0.03	0.03	0.03	0.02	< 0.01	0.04	0.06	0.05	0.01
LOI	23.44	23.88	27.23	17.95	15.29	16.45	19.94	26.87	26.34	24.07	28.61	25.47	28.39	27.95	21.76	20.22
Total	99.68	98.24	99.66	98.57	98.69	100.09	98.56	99.53	98.6	98.73	99.9	100.2	98.92	98.78	98.78	99.65

TABLE 3. Chemical analyses of major elements (wt.%) of altered samples from the Buitrera area.

	Buitrera I					Buitrera II		
	HBI1	HBI2	HBI3	HBI4	HBI5	HBII1	HBII2	HBII3
SiO_2	76.87	74.94	73.7	68.48	71.81	59.89	70.85	76.03
Al_2O_3	13.36	14.48	17.24	18.39	17	15.12	16.32	13.39
Fe_2O_3	0.62	0.57	0.68	1.2	1.12	1.4	1.16	1.1
MnO	0.009	0.009	0.014	0.037	0.044	0.005	0.005	0.005
MgO	0.08	0.1	0.12	0.14	0.15	0.49	0.44	0.12
CaO	0.1	0.19	0.12	0.13	0.16	7.23	0.31	0.13
Na_2O	3.2	2.97	0.74	0.6	0.73	1.3	1.73	4.03
K_2O	3.49	3.31	0.5	0.37	0.48	0.6	1.73	4.19
TiO_2	0.141	0.144	0.193	0.182	0.176	0.068	0.054	0.045
P_2O_5	0.02	0.01	0.01	< 0.01	< 0.01	0.03	< 0.01	< 0.01
LOI	2.52	3.65	7.57	8.69	8.01	14.74	7.4	1.79
Total	100.4	100.4	100.9	98.22	99.69	100.9	100	100.8

instead of kaolinite formed after the dissolution of the glass. There are no Fe or Mn oxides within the halloysite mass which would indicate a continuing flow of water during the time of weathering (Churchman *et al.*, 2010).

Palaeoclimatic studies (Aragón & Romero, 1984) indicate that the climate in the area of the Volcanic Andean Patagonic Province during the upper Palaeocene and lower Eocene was extremely humid and temperate. From the middle Eocene to lower Oligocene the same conditions continued but, towards the middle Oligocene, drier conditions prevailed until the Miocene. Later, as a consequence of the Andean orogeny, desert conditions in Patagonia began. After the Huitrera deposition (Eocene) climatic conditions until the middle Oligocene seem to be favourable for weathering processes, thus constraining the age of alteration to this short period of time.

In Mamil Choique alteration occurred in Group II rocks because they were probably the only ones outcropping at that time. Group I rocks are now recognized through drill holes in the quarries or are exposed after the removal of the clay. Although

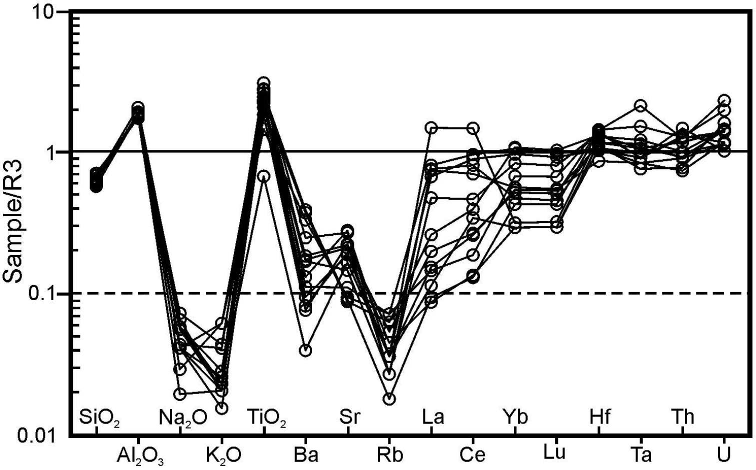

FIG. 10. Mamil Choique altered samples *vs.* R3 (fresh rock from Group II). Alteration is characterized by loss of SiO_2, Na_2O, K_2O, Ba, Sr and Rb; Al_2O_3 and TiO_2 remain immobile. Depletion in *LREE* and enrichment of *HREE* can be observed in some samples.

halloysite is the main alteration product in both areas, the particle morphology is dissimilar. In Mamil Choique spheroidal halloysite predominates over tubular particles, whereas in Buitrera tubular halloysite is the main product with fewer spheroidal particles.

According to several authors, the particle morphology of halloysite appears to be related to the crystallization conditions and geological environment. Pseudo-spherical or spheroidal particles are common in weathered volcanic ashes and pumices. Spheroidal halloysite is related to the saturation state of solutions. Since the dissolution rate of volcanic glass is high, the solution in contact with the glass is likely to be highly supersaturated. Tubular halloysite is commonly derived from crystalline minerals, such as feldspars and micas (Joussein *et al*., 2005).

Adamo *et al.* (2001), studying the weathered pyroclastic material of Roccamonfina volcano in southern Italy, found tubular and spheroidal halloysite in different parts of the same outcrop. From micromorphological observations they concluded that there are differences in the physical nature of the pyroclastic material, with the spheroidal form occurring in more densely compacted material compared to the more loosely packed debris associated with the tubular halloysite. On the other hand, Papoulis *et al.* (2004) reported the appearance of spheroidal, tubular and platy halloysite and kaolinite towards the top of the weathering profile. They concluded that, besides the chemical composition of the ambient solutions which is the main cause of variation in morphology, other factors, such as time, permeability and space availability, may facilitate or determine the formation of a particular type. Halloysite morphology could be related to the original texture of the rocks.

The findings in this paper constraint the morphology of halloysite mainly through its original porosity, and are in agreement with those of Adamo *et al*. (2001). SEM textures show that the spheroidal particles form a densely packed texture (Fig. 3b) and tubular particles show a reduced packing texture (Fig. 3d and f). Where tubes predominate, the texture is very open, with tubes protruding from surfaces toward the centre of hollows (Fig. 3d and f). These results also support part of the conclusions of Papoulis *et al.* (2004) that the permeablility and space available is an important factor in spheroidal or tubular halloysite formation. In Mamil Choique, spheroidal halloysite predominates throughout the profile, and the original rock shows crystaloclasts in a non-porous glassy matrix composed of welded ash shards that have been subjected to high-temperature devitrification. In Buitrera, tubular halloysite is the main alteration product. These rocks show a vapour-phase alteration of glassy material that resulted in total destruction of the original texture (Fig. 2d), where open cavities have been formed as well as feldspars laths, trydimite and spherulites. In some rocks that remain fresh, the cavities are filled with quartz.

Kaolinite has not been found in Buitrera and is present in a small amount in Mamil Choique. Some authors believe that halloysite is transformed into kaolinite with time (Parham, 1969) or over time in favourable chemical conditions (Papoulis *et al.*, 2004). Climatic evidence indicates that after halloysite formation, arid to extremely arid conditions have been established in Patagonia, producing an unfavourable environment for clay mineral formation.

CONCLUSIONS

Three conclusions have been drawn:

(1) Halloysite has been formed by weathering over a time range from middle Eocene to middle Oligocene and extendeding for 50 km in a W–E direction. Persistence of halloysite with time is related to climatic changes to arid conditions after the halloysite formation.

(2) Halloysite is formed independently of the source rock. The requirement is that water is in constant contact with the rock.

(3) Particle morphology depends on the original texture of the rock; spheroidal halloysite is related to rocks with low porosity and tubular particles are related to rocks with open spaces.

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