LATE-NEOPROTEROZOIC HYDROTHERMAL FLUID ACTIVITY IN THE TANDILIA BELT, ARGENTINA

Juan C. MARTÍNEZ[1,2], Jorge A. DRISTAS[1,2], Alfons M. VAN DEN KERKHOF[4], Klaus WEMMER[4], Hans J. MASSONNE[5], Thomas THEYE[5], and María C. FRISICALE[1,2]

[1] Departamento de Geología, Universidad Nacional del Sur. Bahía Blanca, Buenos Aires, Argentina. Email: jcmartin@uns.edu.ar
[2] INGEOSUR-CONICET Bahía Blanca.
[4] Geowissenschaftliches Zentrum der Universität Göttingen, Germany. Göttingen, Germany.
[5] Institut für Mineralogie und Kristallchemie der Universität Stuttgart, Germany. Stuttgart, Germany.

ABSTRACT

In the Barker - Villa Cacique area, Tandilia belt, alteration mineral assemblages were studied by petrography, XRD and EMPA at three different stratigraphic levels: (1) a phyllic alteration at the unconformity palaeoproterozoic basement-neoproterozoic sedimentary succession (TLPU); (2) an advanced argillic alteration in the Las Águilas Formation (middle level); and (3) a phyllic alteration on pyroclastic rocks of the Olavarría Formation (upper level). Special emphasize was placed on the chemical characterization of K-white micas and chlorites. Secondary K-white micas of altered migmatites, from the Las Aguilas and Olavarría Formations have a low paragonite content (Na* <0.13) with a distinctly higher phengite content ($Si/Al_{(tot)}$ ~1.6) in the latter. Secondary Fe-chlorites in arenites at the TLPU and from pyroclastic rocks of the Olavarría Formation have a high Fe/(Fe+Mg) ratio between ~0.80 and 0.88. K/Ar mineral ages (K-white micas and Na-bearing alunite) constrained the hydrothermal fluid flow between *ca.* 590 and 620 Ma, post-dating diagenesis. Illite crystallinity and chlorite geothermometry of altered and dated rocks suggest upward decreasing temperatures from ~350 - 300 ºC to ~250 ºC, markedly higher than the expected diagenetic temperatures and correlative with unlikely deep depths (>9.5 km) for the entire sedimentary pile. Hot fluids would rise from deep-seated realms, metamorphic and/or hidden igneous sources. A correlation with a Brasiliano thermo-tectonic event is hypothesized.

Keywords: *K-white mica and chlorite chemistry, Kübler Index, geothermometry, hydrothermal-diagenetic and metamorphic realms*

RESUMEN

Actividad de fluidos hidrotermales del Neoproterozoico tardío en el cinturón de Tandilia, Argentina.
En el área de Barker - Villa Cacique, Tandilia, se estudiaron mediante petrografía, DRX, y microsonda electrónica, las paragénesis de minerales de alteración de tres niveles estratigráficos diferentes: (1) alteración fílica de la discordancia basamento paleoproterozoico-secuencia sedimentaria neoproterozoica (TLPU); (2) alteración argílica avanzada en la Formación Las Águilas (nivel medio); y (3) alteración fílica en rocas piroclásticas de la Formación Olavarría (nivel superior). Las micas potásicas y cloritas, de dichos niveles de alteración, fueron caracterizadas químicamente. Las micas potásicas de migmatitas alteradas y de las formaciones Las Águilas y Olavarría tienen un bajo contenido en paragonita (Na* <0,13) con un contenido de fengita ($Si/Al_{(tot)}$ ~1,6) especialmente alto en la Formación Olavarría. Las Fe-cloritas en las areniscas de la TLPU y de las rocas piroclásticas de la Formación Olavarría tienen una relación Fe/(Fe+Mg) alta, entre ~0,80 and 0,88. Las edades K/Ar determinadas en micas potásicas y alunitas con sodio limitan la migración de fluidos hidrotermales entre los *ca.* 590 y 620 Ma, luego de la diagénesis de las rocas sedimentarias. La cristalinidad de las illitas y geotermometría de las cloritas de las rocas alteradas y datadas sugieren temperaturas decrecientes hacia arriba en la secuencia estratigráfica, desde los ~350 - 300 ºC a ~250 ºC. Dichas temperaturas son distintivamente mayores que las temperaturas diagenéticas esperables, y correlativas con profundidades extraordinarias (>9,5 km) para el total de la pila sedimentaria. Los fluidos hidrotermales habrían ascendido desde ambientes profundos con una fuente metamórfica y/o cuerpos ígneos ocultos. Una correlación con un evento termo-tectónico Brasiliano es hipotetizada.

Palabras clave: *Química de micas potásicas y cloritas, índice de Kübler, geotermometría, ambiente hidrotermal, diagenético y metamórfico*

INTRODUCTION

In the cratonic sedimentary basin of the Tandilia belt, post-depositional fluid-related processes, such as different stages of diagenesis, very low-grade metamorphism and hydrothermal fluid alteration have been put forward as explanations for the occurrence of diverse secondary mineral assemblages (e.g., Marchese and Di Paola 1975, Zalba *et al.* 1988, Dristas and Frisicale 1992, Frisicale and Dristas 2000, Martínez *et al.* 2006, Dristas and Martínez 2007, Martínez and Dristas 2007, Gómez Peral 2008, Martínez *et* *al.* 2010, Zalba *et al.* 2007, Fernández *et al.* 2010, Gómez Peral *et al.* 2011a, 2011b). As deep-burial diagenesis gradually turns to very low-grade metamorphic conditions between ~200 ºC and 280 ºC (Winkler 1974, Weaver and Broekstra 1984), the determination of crystallization temperatures of diverse mineral assemblages is crucial for a better understanding of fluid-related thermal events. Therefore, for recognition of a hydrothermal alteration not only related textures and typical secondary mineral paragenesis are useful but also estimation of different temperatures of formation between hydrothermal minerals and diagenetic to very low-grade metamorphic minerals.

In the Neoproterozoic Villa Mónica, Cerro Largo and Olavarría Formations of the Olavarría area, four stages of diagenesis (eodiagenesis, early mesodiagenesis deep mesodiagenesis and telodiagenesis), based on the schema proposed by Morad *et al.* (2000) and Worden and Morad (2003), were differentiated from three argillic hydrothermal mineral assemblages (Poiré *et al.* 2005, Gómez Peral *et al.* 2011a, 2011b). The three hydrothermal mineral assemblages with pyrophyllite (Py1, Py2 and Py3) described upwards in the stratigraphy of Villa Mónica and Cerro Largo Formations - pyrophyllite + $2M_1$ illite ± chlorite ± kaolinite ± illite/smectite (Py1); kaolinite + pyrophyllite + ($2M_1$ > 1M) illite + smectite + illite/smectite (Py2) and pyrophyllite + smectite + 1M illite + kaolinite (Py3)- would have been formed at temperatures between >270 ºC and ~150 ºC (Gómez Peral *et al.* 2011a). Such temperature estimations were based on characterization of cements, and clayey matrix and chemical and mechanic compaction fabrics by means of detailed petrographic observations, X-ray diffractometry and SEM.

Evidences of hydrothermal overprint were registered at different stratigraphic levels of the lower sedimentary succession of Barker-Villa Cacique area (100 km southeast of Olavarría). At the Tandilia Late Proterozoic Unconformity (TLPU - Martínez *et al.* 2010) a mineral assemblage indicative of temperatures of ~300 ºC (pyrophyllite + K-rich white mica + Ti-rich hematite < aluminum phosphate-sulfate minerals < tourmaline < anatase-rutile) was described (Dristas *et al.* 2003, Dristas and Martínez 2007, Martínez and Dristas 2007, Martínez *et al.* 2010). At the top of the Villa Mónica Formation and base of the Cerro Largo Formation small iron-ore deposits of hydrothermal origin were described (Dristas and Martínez 2007). At mid-stratigraphic levels of the Sierras Bayas Group, in the Las Águilas Formation, Dristas and Frisicale (1992) recognized conformable and discordant silicified hydrothermal breccias. The wall-rock of these breccias displays an advanced argillic alteration and frequently contains veinlets and lenses of Na-bearing alunite with inclusions of Aluminium-Phosphate-Sulfate minerals (APS) that contain Ba, Sr, REE, Ca and Fe (Martínez *et al.* 2006). Although, a relatively young, middle Permian (*ca.* 250 Ma), different fluid-related telodiagenetic origin for the alunite was proposed (Zalba *et al.* 2007).

According to the aforesaid, two problems that remain unsolved are the determination of the age of the hydrothermal event and the quantitative estimation of temperatures of formation of hydrothermal mineral assemblages. The present work is focused on solving those problems. Therefore, the alteration mineral assemblages from three straigraphic levels of Barker-Villa Cacique were studied for age and geothermometric approaches: (1) altered basement rocks at the lower unconformity (TLPU); (2) altered rocks from the Las Águilas Formation; and (3) an altered rock at the top of the Olavarría Formation. Since K-white micas and chlorites, common mineral phases in the studied alterations, were used for age and geothermometric approches their chemical characterization was also performed.

Kübler Index (KI) is commonly used as a monitor to derive a range of peak temperatures reached in low-grade metamorphic rock (e.g., Kisch 1983, Frey 1987, Eberl 1993, Merriman and Frey 1999, Árkai *et al.* 2003). The strong control of temperature on illite crystallinity was also confirmed in active geothermal fields (e.g., Ji and Browne 2000) and has also been useful to map paleo-fuid flow associated with hydrothermal mineralizations (Xiaofeng *et al.* 2005).

Al tetrahedral occupancy in chlorite structural formulas has proved to be a reliable proxy to determine paleotemperatures of chlorite crystallization in altered rocks at low temperatures (e.g., Cathelineau and Nieva 1985, Cathelineau 1988, Jahren and Aagaard 1989, Jowett 1991, Zang and Fyfe 1995). But, some of the derived empirical calibrations have been questioned based on the effects of mineralogy and bulk-rock composition to chlorite compositional variations other than temperature and pressure (e.g., Velde and Medhioub 1988, Hillier and Velde 1991, De Caritat *et al.* 1993, Essene and Peacor 1995). A general increase in octahedral occupancy is seen with temperature increasing, but a better correlation of tetrahedral Al with temperature suggest that it is less influenced by bulk composition (Hillier and Velde 1991). Recent thermodynamic model of solid solution in chlorites (Vidal *et al.* 2001, Inoue *et al.* 2009) satisfactory evaluate the condition of formation of such minerals, although Fe^{3+} estimation is necessary. De Caritat *et al.* (1993) cautioned about using chlorite geothermometry as a sole method of estimating paleotemperatures. Therefore, temperatures estimated by chlorite geothermometry can be complemented by temperatures estimated from illite crystallinity.

GEOLOGICAL BACKGROUND

Two major units are recognized in the Tandilia belt: the basement, Buenos Aires Complex (Marchese and Di Paola 1975 - here abbreviated as BAC) and a sedimentary succession. The BAC consists predominantly of granitic to tonalitic gneisses, migmatites and granitoids and subordinately of schists, marbles, amphibolites and ultramafic rocks (Cingolani 2011 and references therein). The evolution of the BAC, dated between *ca.*

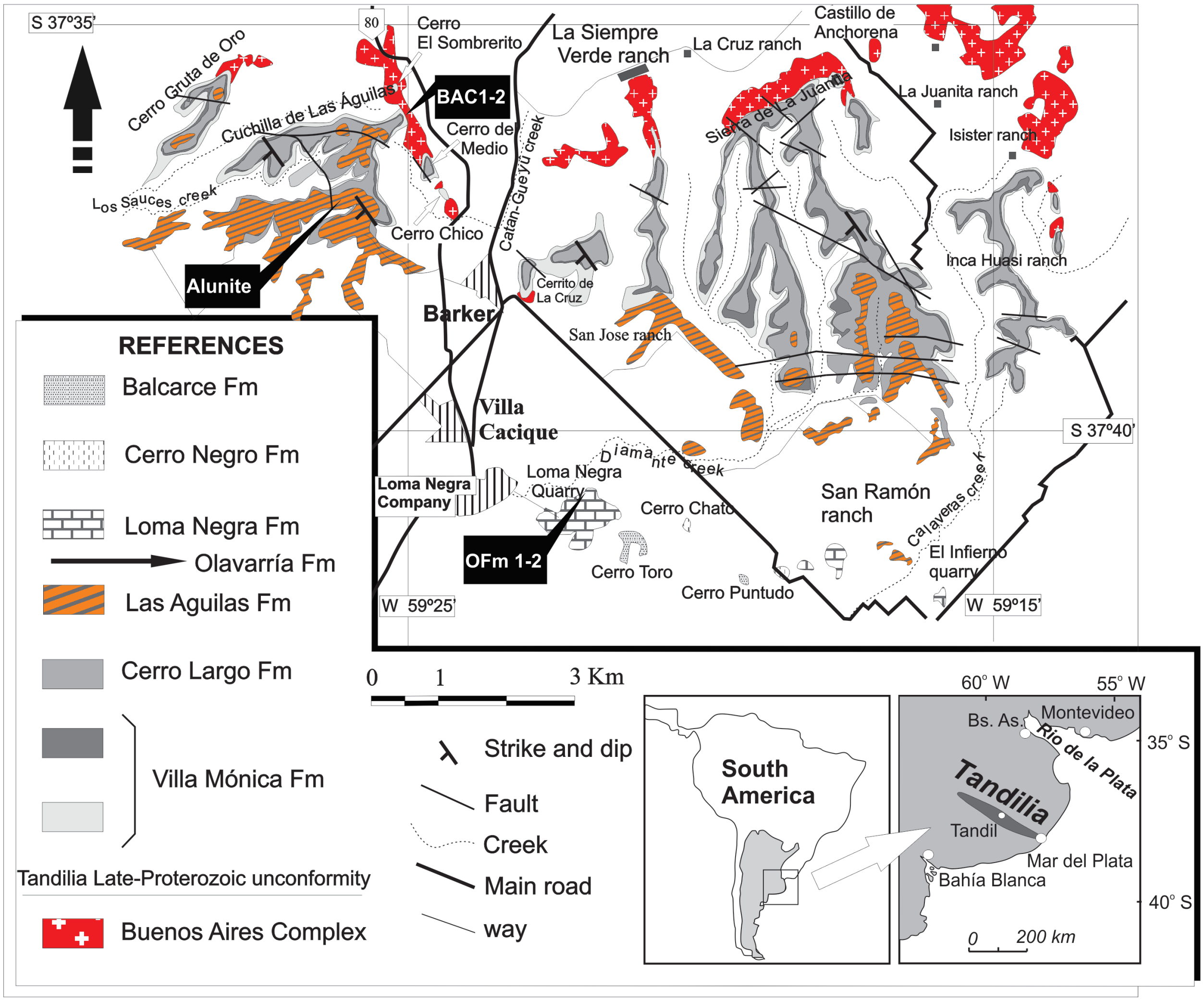

Figure 1: Geological map of the Barker - Villa Cacique area. Locations of dated samples are indicated on the map. Abbreviation: altered Buenos Aires Complex (BAC 1-2), lenses of alunite from the Las Águilas Fm. (Alunite) and altered tuff from top of the Olavarría Fm. (OFm 1-2).

2200-1600 Ma, is mainly related to the Transamazonian cycle with late intrusions of early Proterozoic tholeiitic dykes (e.g., Cingolani and Dalla Salda 2000, Hartmann *et al.* 2002, Iacumin *et al.* 2001, Teixeira *et al.* 2002). This basement rocks are unconformably overlain by a shallow marine siliciclastic-carbonate sedimentary succession with minor pyroclastic components (Dristas and Frisicale 1987, Poiré and Spalletti 2005, Zimmermann *et al.* 2011). A widely accepted stratigraphic unit division, summarised in table 1, comprises from base to top: the Sierras Bayas Group (Dalla Salda and Iñiguez-Rodriguez 1979, Poiré 1993), the youngest Neoproterozoic unit, the Cerro Negro Formation (Iñiguez-Rodriguez and Zalba 1974) and the early Palaeozoic Balcarce Formation (Dalla Salda and Iñiguez-Rodriguez 1979). In recent works several stages of diagenesis were recognized in the Sierras Bayas Group of the Olavarría area, 100 km to the northwest of Barker. Paleotemperatures and depths of peak diagenetic conditions were estimated in rocks of the Sierras Bayas Group of Olavarría area, unaltered by hydrothermal fluids. The lowermost sedimentary units (Villa Mónica Formation) have reached a very deep mesodiagenetic regime (~200 ºC and depths of 5 - 6 km), Cerro Largo Formation an intermediate mesodiagenetic regime (~150 ºC and depths < 4 km) and the Olavarría Formation an early mesodiagenetic regime (<100 ºC and depths < 3 km) (Gómez Peral 2008, Gómez Peral *et al.* 2011a). In the Barker-Villa Cacique area, the complete sedimentary succession is thinner than in the Olavarría area, less than 150 m thick. The entire succession shows a slightly variable general dip of 3-6º to the southwest. Subvertical faults of <5 km with east-west and northwest-southeast strike directions define a block structure with a relatively higher tectonic position of the northern blocks (Fig. 1). Geophysics reveals that the same east-west, northeast-southwest and secondary northwest-southeast alignments characterize the block structure of the continental crust of the Tandilia belt (Kostadinoff 1995).

East of Cuchilla de las Águilas, Cerro El Sombrerito, Cerro del Medio and Cerro Chico hills (Fig. 1), the basement consists of banded migmatites with local in-

TABLE 1: Stratigraphic schema for the Tandilia belt (taken and modified from Poiré and Spalletti 2005).

Ages	NW REGION (Olavarría)		CENTRAL REGION (Barker – Villa Cacique)	SE REGION (Mar del Plata)	Brief lithology description
Ordovician – Cambrian	Balcarce Fm.		Balcarce Fm.	Balcarce Fm.	Highly cemented quartz arenites with claystone and conglomeradic lenses.
600? Ma				Punta Mogotes Fm.	Metapelites, metasiltstones and metasandstones.
	Cerro Negro Fm.		Cerro Negro Fm.	?	Siltstones, claystones and marls, interbedding of scarce fine-grained sandstones.
	Sierras Bayas Group	Loma Negra Fm.	Loma Negra Fm.		Coarse grained and fine grained micritic limestones.
		Olavarría Fm.	Olavarría Fm.		Claystones and siltstones.
Neo-Proterozoic			Las Águilas Fm.		Silicified breccias reddish to whitish clays and alternating succession of claystones – siltstones and quartz – rich sandstones.
		Cerro Largo Fm.	Cerro Largo Fm.		Breccias, highly cemented quartz arenites, clays and claystones.
800 Ma		Villa Mónica Fm.	(Villa Mónica Fm. = La Juanita Fm.)		Bimodal to unimodal quartz arenites, minor wackstones and orthoconglomerades. Dolostone, clays and claystones on its upper section.
Palaeoproterozoic to Mesoproterozoic	Buenos Aires Complex **(BAC):** Undifferentiated igneous – metamorphic basement				

terbedded amphibolite lenses of <1.5 m wide and up to 20 m long. The rocks show subvertical WNW - striking foliation (N70°W to N60°W). The leucosome of the migmatites consists of quartz, plagioclase (andesine), orthoclase and scarce microcline, whereas biotite dominates in the melanosome. Accessory minerals include garnet, apatite, zircon, allanite and monazite (Martínez *et al*. 2010).

The lower section of the sedimentary succession (Villa Mónica, Cerro Largo and Las Águilas Formations) is predominantly composed of quartz arenites with subordinate intercalations of clay and claystones, small iron-ore deposits, silicified breccias, and one dolostone layer less than 2 m thick. The upper part of the sedimentary sequence (Olavarría, Loma Negra and Cerro Negro Formations, outcrop in the Loma Negra quarry at Villa Cacique) is mainly composed of limestones, marls and siltstones (Fig. 1 and Table 1).

Several radiometric ages were obtained for the sedimentary succession of the Tandilia belt (e.g., Bonhomme and Cingolani 1980, Cingolani and Bonhomme 1988, Dristas and Martínez 2007). In the Olavarría area, claystones of the Olavarría Formation (or Cerro Largo Formation) overlain by limestones showed an Rb/Sr isochron of 769 ± 12 Ma with a KI of diagenetic signature (Bonhomme and Cingolani 1980). In the same area, Cingolani and Bonhomme (1988) determined an Rb/Sr isochron with an age of 793 ± 32 Ma in claystones of the basal sedimentary succession of the Sierras Bayas Group (top of Villa Mónica Formation). Stratigraphically equivalent claystones from the Barker area showed a bulk rock K/Ar age of 787 ± 22 Ma interpreted as diagenetic (Dristas and Martínez 2007). The age of the limestones from the Loma Negra Formation was constrained by considering the secular $^{87}Sr/^{86}Sr$-ratio variation curve for Neoproterozoic and Early Cambrian seawater as proposed by Gorokhov *et al*. (1995). The best estimate for a Loma Negra "Sr sea" was found to be 0.70584 ± 0.0001, indicating an age of deposition *ca*. 800 Ma (Kawashita *et al*. 1999). In the same way, the aforementioned authors determined an age of 734 ± 4 Ma for the overlying Cerro Negro Formation based on Rb-Sr isotopes of clay minerals which were isotopically homogenized during diagenesis in the Olavarría area. In addition, K/Ar analysis applied to fine fractions (<2 µm) from the Cerro Negro Fm. of the Loma Negra Company quarry at Villa Cacique showed an average age of 680 Ma with KI belonging to the anchizonal field (Cingolani *et al*. 1991). This age represents the minimum age of deposition since possibly inherited ages of detrital micas were not completely homogenized during a thermotectonic event (Cingolani *et al*. 1991). All previous radiometric ages therefore appear to indicate that the entire sedimentary succession (Sierras Bayas Group plus the Cerro Negro Formation) is older than late Neoproterozoic (Ediacaran). Conversely, reinterpretation of the data of Kawashita *et al*. (1999) gives rise to an age of 580-590 Ma (Ediacaran) for the sedimentation of the Loma Negra Formation (top of Sierras Bayas Group) in the area of Olavarría (Gómez Peral *et al*. 2007)

ANALYTICAL METHODS

More than 120 samples of different types of altered and fresh rocks were collected during several annual field trips and investigated by transmitted-light microscopy during the development of a PhD thesis (Martínez 2009). Agate-mill powdered samples were used for fine-grained mineral identification by means of a Rigaku-Denki Geiger Flex Max III C X-ray diffractometer at the Departamento de Geología (UNS), Bahía Blanca, Argentina. The spectrometer was computerized with the MDI DataScan 4 software. Setup conditions for analysis of X-ray diffractometry (XRD) of powdered samples were: 35 kV, 15 mA and step scanned from 3 to 65º 2θ, 0.04º 2θ/s for routine procedure. Some samples, treated with ethylene glycol for the identification of expansible clay minerals, were performed from 3 to 30º 2θ and 0.01º 2θ/s.

Sample preparation and Kübler Index measurements

Four selected whole-rock samples of 1 - 2 kg, two of altered basement (BAC 1-2) from the east tip of Cuchilla de las Águilas (Fig. 1) and the others two from an altered pyroclastic rock on top of the Olavarría Formation (OFm 1-2) from the Loma Negra quarry (Fig. 1), were taken for separation of fine mineral fractions, <2 µm and <0.2 µm. These fractions were used for K/Ar age and Kübler Index (KI) determinations on K-white mica. The rocks were crushed and ground in a shatter vibration mill (for 10 to 20 s) and split into fractions of >63 µm and <63 µm. From the latter fraction the clay fractions of <2 µm were extracted by differential settling (Atterberg method). A second <2 µm fraction was acquired in the same way and used to separate the fractions of <0.2 µm with an ultra-centrifuge. The different fine fractions were examined by XRD and Kübler Index (KI).

For the KI, texture compounds were prepared using 1.5-2.5 mg/cm^2 of sample material (Weber 1972). The full width at half maximum (FWHM) of the 10-Å peak was determined using a software developed at the University of Göttingen. Digital measurement of KI was carried out by the step-scan method (301 points, 7 - 10° 2θ, scan step 0.010° 2θ, integration time of 4 s, receiving slit of 0.1 mm, automatic divergence slit) on a Philipps PW 1800 diffractometer. All samples were investigated in duplicate. The measurements were carried out in 'air dry' and 'glycolated' media in order to detect expandable layers of smectite-type minerals.

KI-values are given in (Δº2θ). The limits for diagenesis/anchizone and anchizone/epizone are 0.600° to 0.400° and 0.240° Δº2θ, respectively. These limits were checked in the interlaboratory standardization program of Warr and Rice (1994). The given KI-values are nearly identical to the crystallinity index standard (CIS).

Analytical procedure for K/Ar dating of alunite and K-white micas

K/Ar dating of one sample composed of > 95% Na-bearing alunite (< 5% quartz, nacrite, hematite), from the quarries of western Barker (Fig. 1), was performed at Activation Laboratories Ltd. (Actlabs), Ancaster, Ontario, Canada. The potassium concentration was assessed by ICP and the argon analysis was performed using the isotope dilution procedure on a noble gas mass spectrometer. The procedure for Ar analysis as provided by Actlabs was the following: an aliquot of the sample was weighed into an Al container, loaded into the sample system of the extraction unit and degassed at ~100 ºC during 2 days to remove the surface gases. Argon was extracted from the sample in a double vacuum furnace at 1700 ºC and the argon concentration was then determined using isotope dilution with ^{38}Ar spike, which was introduced to the sample system prior to each extraction. The extracted gases were cleaned up in a two-step purification system. The pure Ar was introduced into a customer-built magnetic sector mass spectrometer (Reynolds type) with a Varian CH5 magnet. The ion source has an axial design (Baur-Signer source) which provides more than 90% transmission and extremely small isotopic mass-discrimination. The measurement of Ar isotope ratios was corrected for mass-discrimination and then atmospheric argon was removed assuming that ^{36}Ar was only from the air. The concentration of ^{40}Ar radiogenic was calculated by using a ^{38}Ar spike concentration. After each analysis the extraction temperature was elevated to 1800 ºC for a few minutes and the furnace was prepared for next analyses. For the K-analysis, an aliquot of the sample was weighed into a graphite crucible with lithium metaborate/tetraborate flux and fused using LECO induction furnace. The fusion bed was dissolved with acid. The standards, blanks and samples were analyzed on a Varian 735 ICP spectrometer.

K/Ar dating of K-white micas was carried out at the Geowissenschaftliches Zentrum, University of Göttingen, Germany. The argon - isotopic composition was measured in a pyrex glass extraction and purification line coupled to a VG 1200 C noble - gas mass spectrometer operating in static mode. The amount of radiogenic ^{40}Ar was determined by the isotope-dilution method using a highly enriched ^{38}Ar spike from Schumacher, Bern (Schumacher 1975). The spike was calibrated against the biotite standard HD-B1 (Fuhrmann *et al.* 1987). The age calculations were based on the constants recommended by the IUGS quoted in Steiger and Jäger (1977).

Potassium was determined in duplicate by flame photometry using an Eppendorf Elex 63/61. The samples were dissolved in a mixture of HF and HNO_3 according to the technique of Heinrichs and Hermann (1990). CsCl and LiCl were added as an ionisation buffer and internal standard, respectively. The analytical error for the K/Ar age calculations is given on a 95% confidence level (2σ). Details of argon and potassium analyses for the laboratory procedures in Göttingen are given in Wemmer (1991).

Electron microprobe (EMP) analyses

More than 30 samples of different lithologies from the argillized basement east of the Cuchilla de la Águilas range, different lithologies of the Las Águilas Formation and the top of Olavarría Formation in the quarry of the Loma Negra Company (Fig. 1) were selected and analyzed with a Cameca SX 100 electron microprobe at the Institut für Mineralogie und Kristallchemie, University of Stuttgart, Germany. The results of this technique of study presented in this work are part of the unplublished PhD Thesis by Martínez (2009). Wavelength-dispersive spectrometry (WDS), energy dispersive spectrometry (EDS), backscattered imaging and X-ray element mapping allowed the tiny mineral phases and microtextures to be identified and characterized. The experimental conditions were selected according to the analyzed minerals in order to minimize devolatization. A voltage of 15 kV was combined with a beam current between 7 and 10 nA, take-off angle of 40º and a variable spot-beam diameter of ~2-3 μm. Concentrations of Na, K, Ti, Mg, Mn, Fe, P, Ca, Si, Al and Ba were determined with five spectrometers with counting times of 20 s at the corresponding Kα (Lα for Ba) peak. Reference material for quantification and calibration of EMP were natural and synthetic standards.

Chemical analyses of K-white micas with total oxides >90 %, Si (a.p.f.u.) >6.00, total K+Na+Ca >1.6 and Ca (a.p.f.u.) <0.01 were considered suitable. Taking into account that the studied micas are associated with iron oxides, Fe^{3+} was arbitrarily assumed to be total iron (Martínez *et al.* 2010). Structural formulas of K-white micas were calculated based on 22 oxygens. Structural formulas derived from chlorite EMP analyses were calculated based on 28 oxygens and assuming total iron as Fe^{2+}, since trivalent iron generally constituted less than 5% of total iron (Cathelineau and Nieva 1985, Hillier and Velde 1991). Significant contents of Na, K, or Ca in chlorite analyses suggest that it is interestratified and/or electron beam contamination with neighbouring mineral phases and therefore analyses with > 0.5 wt. % of total Na$_2$O+CaO+K$_2$O must be discarded (Velde and Medhioub 1988, Hillier and Velde 1991).

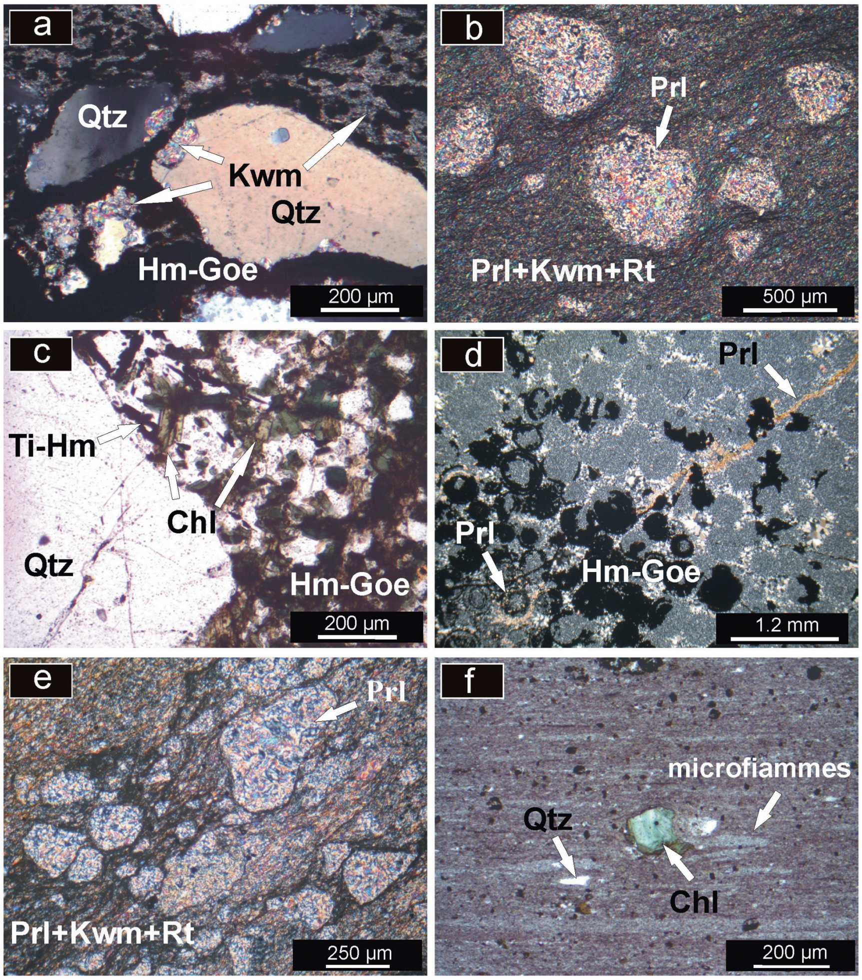

Figure 2: Petrographic photomicrographs. Altered sandstones of the base of the Villa Mónica Fm. at the TLPU in different localities (a-c). a) Quartz clast with caries and replacement by Kwm in a groundmass of Kwm + Goe-Hm, north of Cerro del Medio hill, west of Barker (crossed polars). b) Complete psedomorphic replacement of quartz clast ("ghost clast") by Prl, range of La Siempre Verde ranch (crossed polars). c) Bimodal quartz arenites with intergranular Chl, Ti-Hm and Hm-Goe, southwest of Cerro Chico hill, west of Barker (parallel light). Lithofacies at Las Águilas Fm. (d-e). d) Oolithic texture of massive secondary quartz with solid inclusion and veinlets of Prl (crossed polars). e) Pyrophyllite pseudomorph after quartz-clast ("ghost clast") in a groundmass of Prl+Kwm+Rt, whitish clays (crossed polars). f) Altered pyroclastic rock with chlorite after mafic (biotite?) in a fine-grained K-white mica groundmass, upper section of the Olavarría Fm., Loma Negra quarry (parallel light). Abbreviations: Chlorite (Chl), goethite (Goe), hematite (Hm), K-white mica (Kwm), pyrophyllite (Prl), quartz (Qtz), rutile (Rt), Titanium-hematite (Ti-Hm).

DESCRIPTION OF ALTERED STUDIED ROCKS

Alteration at the Tandil Late-Proterozoic Unconformity (TLPU)

A variable metre thick (5 - 15 m) alteration zone with a generalized common pattern of alteration composed of: (1) K-white mica + chlorite + calcite + rutile + hematite/goethite farther from the unconformity and (2) K-white mica + pyrophyllite + paragonite/intermediate K-Na mica + rutile + hematite/goethite + Aluminium Phosphate-Sulphate (APS) minerals + tourmaline ± kaolinite closer to the unconformity was described in detail at the Tandilia Late Proterozoic Unconformity (TLPU) (Dristas *et al.* 2003, Dristas and Martínez 2007, Martínez and Dristas 2007, Martínez *et al.* 2010).

The altered migmatite samples selected for K/Ar dating (BAC 1 - 2) are dominated by a groundmass of sericite (2M$_1$), rutile, tourmaline and APS minerals ± goethite-hematite. Crystals of granoblastic quartz with marked dissolution embayments (caries) of the most altered basement are, together with zircon, the only preserved minerals (Martínez *et al.* 2010). Backscattered and EMP analyses on sandstones of the base of the Villa Mónica Formation were useful for determining quartz clast replaced dominately by pyrophyllite or K-white micas and a groundmass of pyrophyllite + K-white mica or only K-white mica (Martínez *et al.* 2010). The latter is exemplified in figures 2a - b. But, at the base of the Villa Mónica Formation bimodal quartz arenite with the mineral assemblage kaolinite + Fe-chlorite + Ti-specularite + goethite + rutile (Fig. 2c) might be present. Such chlorites were chemically characterized and used for geothermometric determinations (Table 3a-b and Fig. 4c-d).

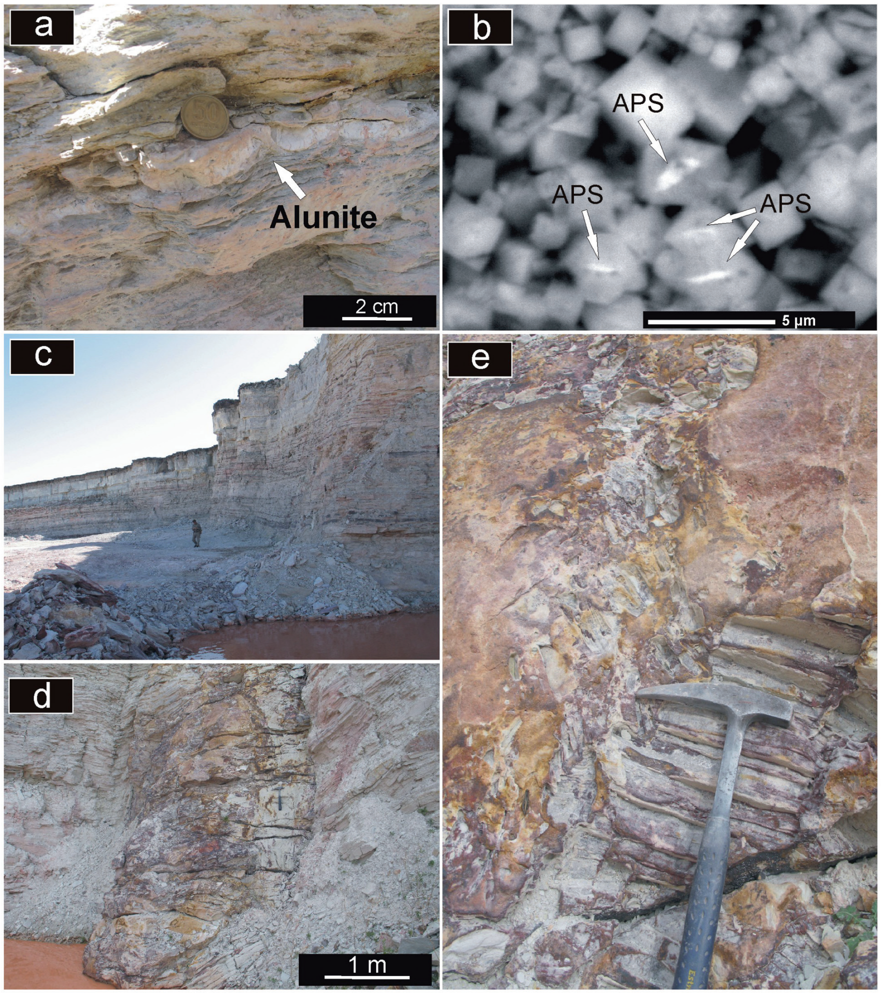

Figure 3: a) Lenses of alunite in whitish clays of Las Águilas Fm. b) Pseudocubic Na-alunite with cores of APS minerals. c) Upper lithofacies with interbedding of clays and quartz-rich arenites, and massive quartz arenite on top. d) Hydrothermal breccias cross-cutting clays and sandstones of the hydrothermally overprinted unit. e) Detail of tabular broken clats of quartz arenites of wall-rock included in discordant breccias.

Alteration at Las Águilas Formation

The Las Águilas Formation exclusively outcrops in the Barker - Villa Cacique area, overlaying the Cerro Largo Formation (Poiré and Spalletti 2005). Three lithofacies were identified from base to top (Zalba *et al.* 1988): breccias (lower lithofacies), claystones and mudstones (middle lithofacies) and alternating claystone, siltstone, and sandstone sediments (upper lithofacies) (Fig. 3a). Massive quartz arenite and quartz- oligomictic conglomerate layers on top of the last lithofacies are included in the same unit (Poiré and Spalletti 2005). The lower lithofacies of the Las Águilas Formation has a variable thickness, up to ~5 m, due to its lens-like morphology (Dristas and Frisicale 1992). It is composed of massive saccharoidal quartz (chert) and silicified breccias with clasts of saccharoidal quartz, clays and laminated quartz arenites. A scarce matrix in the breccias is composed of monocrystalline and polycrystalline aggregates of quartz and a groundmass of pyrophyllite, sericite and dickite. Under the petrographic microscope, both massive quartz and quartz clasts of the breccias are microcrystalline and contain sandstone quartz clasts with corroded overgrowths of preexisting diagenetic cement. This microcrystalline quartz, massive and of breccia clasts, often display an oolithic texture (Fig. 2d) mainly composed of rhythmic and concentric microcrystalline quartz bands, but also goethite-hematite and pyrophyllite (Dristas and Frisicale 1992). The latter mineral has also been recognized in veinlets (Fig. 2d) pointing to in situ crystallization, in divergence with a possible detrital origin (Zalba *et al.* 1982). The middle lithofacies show massive, laminated or convolute laminated structure (Zalba *et al.* 1988). Pyrophyllite, K-white micas and part of kaolinite, together with quartz and traces of feldspar were considered to be detrital, derived from the altered basement; whereas, alunite, some kaolinite, halloysite, goethite and diaspore would have a diagenetic origin (Zalba *et al.* 1982, Zalba *et al.* 1988). It is worth to mention that feldspar was neither recognized in any petrographic section nor in XRD of our samples. The finding of quartz grains with corroded rims until its complete replacement by pyrophyllite (Fig. 2e), rutile crystals delineating vesiculation of pumicite fragments and the associated mineral assemblage led to the interpretation of epiclastic and pyroclastic rocks overprinted by hydrothermal alteration (Dristas and Frisicale 1983, Dristas and Frisicale 1992).

Regarding to this, a detailed description of alunite lenses and veinlets as well as APS minerals occurrence is depicted in Martínez et al (2006). The latter authors determined that whitish lenses and veinlets, such as the one shown in figure 3a, mostly correspond to pseudocubic Na-bearing alunites $((K_{0.54}, Na_{0.35}) (Al_{3.03}) (SO_4)_2)$. Aluminium Phosphate-Sulfate (APS) minerals were identified as isolated crystal immersed in the pyrophyllitic-kaolinitic groundmass and as core inclusions into those Na-bearing alunite crystals (Fig. 3b). These authors determined that the chemistry of APS minerals included in Na-bearing alunite are between the florencite and svanbergite members of the woodhouseite and crandallite series. Likewise, chemistry of APS minerals of Las Águilas Formation points to Ce-florencite to svanbergite members (Zalba *et al.* 2007).

Upwards, up to 9 m of interbedding between quartz-rich arenites and whitish to greenish clays characterized the upper lithofacies (Fig. 3c). In the lower section of this lithofacies, pyrophyllite, K-white mica and kaolinite fill interspaces among corroded quartz grains, where kaolinite and pyrophyllite seem to be intergrown. K-white micas of this corroded caries were chemically characterized (Fig. 4a-b) A lessening of clay fraction is correlative with pyrophyllite and kaolinite disappearance to the upper levels (Zalba *et al*. 1988). Veinlets of idiomorphic apatite crystals and opal were identified in backscattered images of samples from the upper section of this unit (quarries at ~10 km to the east of Barker), but no spatial relationship was observed between APS-minerals and secondary apatite.

Vertical dikes of ~4 m wide cross cut the entire middle and upper lithofacies of the Las Águilas Formation (Fig. 3d-e). These vertical features would be related to horizontal breccias defined together as hydrothermal breccias (Dristas and Frisicale 1992). Other deformational features, such as folding of this unit, are common, and may allow fluid in the rocks to flow out.

Alteration of the top of the Olavarría Formation

This unit was described by Andreis et al (1996) in the Olavarría area, approximately 100 km NW of the study area. A small outcrop (less than 2.5 m thick) of the uppermost section of the Olavarría Formation is exposed in the quarry of Loma Negra Company at Villa Cacique (Fig. 1). It is a green to dark purple clay-rich level of ~0.80 m thick showing fine lamination. Under the petrographic microscope this rock displays aligned phenoclasts floating in a laminar matrix of potassic white mica (<10 µm)(Fig. 2f). The phenoclasts were identified as corroded monocrystalline and polycrystalline quartz, chloritized biotite and idiomorphic sanidine (< 5% vol.) and plagioclase (>20 µm), partly replaced by calcite. Microfiammes composed of fine-grained aggregates of quartz and K-white mica goethite-impregnated suggest that this rock corresponds to an altered welded tuff. Chlorite aggregates (<5 % vol.) along flow lines denote the existence of broken biotite laths probably due to the high viscosity of the flow. Backscattered images and WDS analyses point to tiny idiomophic apatite crystals with REE contents in this rock. The rock is crosscut by thin, up to 1.5 cm wide, dikes of fine-grained quartz arenite without sedimentary structures and not showing any relationship with tectonic features probably intruded as liquefied sand as a result of overpressured fluids.

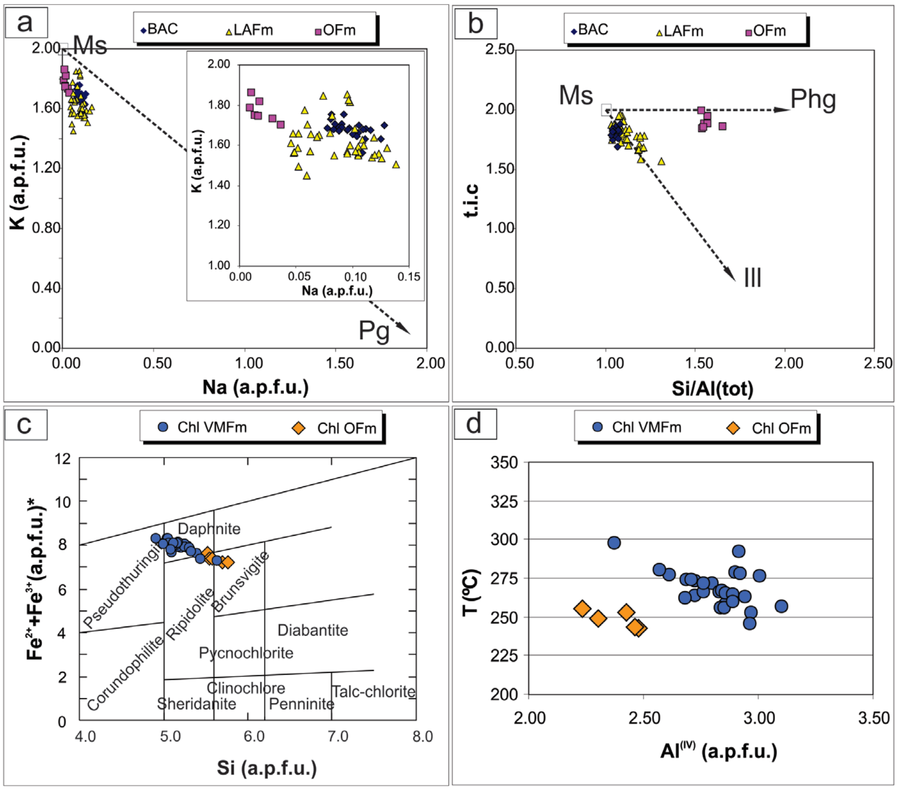

Figure 4: Compositional variation of cations and ratios of dioctahedral K-white micas from the altered basement of Cuchilla de las Águilas (BAC- data from Martínez *et al*. 2010), Las Aguilas Fm. (LAFm) and Olavarría Fm. (OFm) and chlorites from Las Aguilas Fm. (Chl LAFm) and Olavarría Fm. (Chl OFm). In a and b, empty squares and dashed lines respectively indicate the theoretical muscovite position and corresponding exchange vectors. a) Variation plot of K (a.p.fu.) – Na (a.p.f.u.) (blow up in the same plot). b) Variation plot of Si/Al(tot) – t.i.c. considering the Ms-Ill and Ms-Phg tie lines. c) Classification of chlorites from the base of the Villa Mónica Fm. (VMFm) and Olavarría Fm. (OFm) based on chemistry variation. d) Temperatures estimated in chlorites from the base of Villa Mónica Fm. (VMFm) and Olavarría Fm. (OFm) based on tetrahedral Al and Fe/(Fe+Mg) ratio of Zang and Fyfe (1995)`s equation. Abbreviations: muscovite (Ms), paragonite (Pg), phengite (Phg) and illite (Ill). t.i.c. = total interlayer charge = K+Na+2Ba+2Ca per formula unit. Fe^{2+}(tot) (a.p.f.u.)* = Fe^{2+} +Fe^{3+} (a.p.f.u.).

CHEMISTRY OF K-WHITE MICAS AND CHLORITES

Representative EMP analyses of K-white micas of the alteration of the basement, the Olavarría Formation and of the Las Águilas Formation are shown in table 2. Analyses of K-white micas of the altered basement at the east of Cuchilla de las Águilas (Fig. 1) are those presented by Martínez et al (2010), re-examined for the purposed of comparison. Micas from the altered BAC and Olavarría Formation (BAC 1-2 and OFm 1-2) were those selected for K/Ar dating of fine fractions. Divariant diagrams, K (a.p.f.u.) vs. Na (a.p.f.u.) and t.i.c. vs. Si/Al (tot) were used to chemically characterize such micas, considering the compositional exhange vectors of illite, paragonite and pyrophyllite by possible substitutions in muscovite. Based on the classification schema proposed by the IMA subcommittee report (Rieder *et al*. 1998), the K-white micas of the altered rocks of basement and base of the sedimentary succession of the Barker - Villa Cacique area are true micas and dioctahedral micas (Martínez *et al*. 2010). Some K-white micas of the al-

TABLE 2: Representative electron microprobe analyses of K-white mica (Kwm) from the altered BAC, Las Aguilas Fm. (LAFm) and Olavarría Fm. (OFm). K-white micas are based on 22 oxygens. Total Fe is considered Fe^{3+}.

Mineral	Kwm BAC						Kwm LAFm		Kwm OFm									
Anal. nº	2	8	16	17	19	25	1	4	7	33	2	5	14	16	17	18	22	23
Samples	09041003						17181006		05191005		08191005		01181006					
SiO_2	46.61	45.34	45.22	45.77	45.83	45.63	48.23	49.20	48.51	46.76	49.21	48.05	47.22	51.25	51.13	51.62	52.51	50.28
TiO_2	0.04	0.11	0.11	0.04	0.02	0.04	0.01	0.04	0.01	0.26	0.03	0.17	0.42	0.30	0.31	0.21	0.26	0.33
Al_2O_3	37.11	36.90	36.81	37.29	35.96	37.20	36.77	35.49	37.94	36.71	35.34	33.54	31.85	28.07	27.65	28.44	26.94	27.78
Fe_2O_3	1.19	1.52	1.57	1.26	1.90	1.43	0.31	0.38	0.72	1.21	1.00	3.33	6.16	5.52	5.85	5.01	5.23	5.69
MnO	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.00	0.00	0.00	0.00	0.00
MgO	0.12	0.03	0.05	0.00	0.13	0.08	0.28	0.33	0.28	0.94	0.57	1.01	0.95	1.91	1.95	1.87	1.85	1.90
BaO	0.00	0.05	0.02	0.01	0.05	0.04	0.21	0.15	0.13	0.03	0.05	0.11	0.06	0.27	0.21	0.19	0.27	0.29
CaO	0.07	0.07	0.06	0.02	0.04	0.03	0.01	0.01	0.09	0.00	0.10	0.06	0.00	0.04	0.00	0.00	0.03	0.00
Na_2O	0.43	0.35	0.30	0.50	0.36	0.45	0.32	0.27	0.56	0.38	0.19	0.25	0.21	0.12	0.03	0.05	0.14	0.04
K_2O	9.28	10.00	9.87	10.04	10.29	9.88	10.00	9.87	9.22	11.17	9.43	9.87	10.79	10.41	10.71	10.55	10.23	11.05
Total	**94.85**	**94.37**	**94.02**	**94.93**	**94.58**	**94.78**	**96.14**	**95.74**	**97.46**	**97.46**	**95.92**	**96.41**	**97.69**	**97.89**	**97.84**	**97.94**	**97.46**	**97.36**
Si	6.147	6.058	6.059	6.07	6.125	6.061	6.277	6.414	6.208	6.083	6.396	6.307	6.689	6.693	6.714	6.670	6.856	6.639
AlIV	1.853	1.942	1.941	1.929	1.875	1.939	1.723	1.586	1.792	1.917	1.604	1.693	1.311	1.307	1.286	1.330	1.144	1.361
AlVI	3.915	3.869	3.873	3.901	3.792	3.886	3.918	3.868	3.930	3.714	3.810	3.498	3.007	2.958	3.074	2.986	3.001	2.962
Ti	0.004	0.011	0.011	0.004	0.003	0.004	0.001	0.004	0.001	0.026	0.003	0.016	0.029	0.030	0.020	0.035	0.026	0.033
Fe^{3+}	0.118	0.153	0.158	0.126	0.191	0.143	0.030	0.037	0.069	0.118	0.098	0.329	0.542	0.577	0.491	0.563	0.514	0.565
Mn	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.00	0.00	0.000	0.002	0.00	0.00	0.00	0.00	0.000	0.000
Mg	0.023	0.005	0.010	0.000	0.026	0.015	0.055	0.065	0.054	0.183	0.111	0.197	0.373	0.381	0.362	0.376	0.360	0.373
Total VI	4.060	4.038	4.053	3.904	3.820	4.048	4.004	3.974	3.985	3.922	4.022	4.042	3.951	3.946	3.947	3.960	3.387	3.368
Ba	0.000	0.011	0.004	0.001	0.010	0.008	0.044	0.030	0.026	0.006	0.010	0.023	0.056	0.044	0.040	0.042	0.055	0.061
Ca	0.010	0.011	0.008	0.003	0.006	0.005	0.002	0.001	0.012	0.00	0.014	0.009	0.006	0.000	0.000	0.004	0.004	0.000
Na	0.109	0.090	0.078	0.128	0.093	0.116	0.080	0.069	0.138	0.096	0.048	0.063	0.029	0.009	0.013	0.017	0.036	0.010
K	1.561	1.706	1.688	1.700	1.756	1.675	1.660	1.642	1.505	1.854	1.563	1.654	1.733	1.788	1.751	1.747	1.705	1.862
t.i.c.	1.690	1.839	1.790	1.836	1.880	1.816	1.832	1.772	1.720	1.960	1.659	1.782	1.885	1.884	1.844	1.856	1.859	1.993
Na*	0.065	0.050	0.044	0.070	0.050	0.065	0.046	0.040	0.084	0.049	0.029	0.037	0.017	0.005	0.008	0.009	0.021	0.005
Si/Al(tot)	1.066	1.043	1.042	1.041	1.081	1.041	1.113	1.176	1.085	1.080	1.181	1.215	1.549	1.569	1.540	1.546	1.654	1.536

tered basement display variable Na* = Na/(Na+K+Ca), of up to 0.45 (formulae based on 11 oxygens), leading the abovementioned authors to suggest the possible interlayering of K-Na-bearing micas and paragonite in these dioctahedral micas. K-white micas of altered basement from east of Cuchilla de las Águilas are typified as having Na* contents below 0.07, slightly variable Na (a.p.f.u.) between 0.08 - 0.13 (low paragonite content), total interlayer cation (t.i.c. = K+Na+2Ba+2Ca) ranging from 1.7 to 1.85, and low illitic and phengitic content (Fig. 4a-b).

The chemistry of K-white micas of the quartz-rich sandstones of the lowermost upper lithofacies of the Las Águilas Formation is displayed in figure 4a-b. These micas compose an intergranular clay mineral assemblage, pyrophyllite + kaolinite + muscovite, of the hydrothermally overprinted sandstones. K-white micas have K (a.p.f.u.) between 1.45 and 1.85 and Na (a.p.f.u.) between 0.04 and 0.14, slightly more variable than the K-white mica values for the altered basement (Fig. 4a). A more widespread illitic substitution is seen when K-white micas of the Las Águilas Formation are compared with those of the altered BAC, in t.i.c. vs. Si/Al (tot) (Fig. 4b).

The altered tuff of the top of the Olavarría Formation was selected for the K/Ar dating of the K-white mica fine fraction. In these white micas the interlayer position is almost exclusively filled by potassium, K (a.p.f.u.) values between 1.73 and 1.86, with t.i.c values higher than 1.75 up to 2.00 (low vacancies). Si content is markedly higher than in the other two analyzed groups of K-white micas and has a low variation around ~6.7; the Si/Al(tot) ratio indicates a phengitic substitution (Fig. 4b). After Al, Fe is the main cation in an octahedral position with variable values between 0.49 and 0.57 (a.p.f.u.).

Chlorites of two altered rock types were studied: (1) altered bimodal quartz arenites from the base of the Villa Mónica Formation (at the TLPU) in one of the hills (Cerro Chico) west of Barker (Fig. 2c) and (2) altered pyroclastic rocks from the top of the Olavarría Formation in the Loma Negra quarry of Villa Cacique (Fig. 2f). Chlorites of the altered quartz arenites were previously described by Dristas and Martínez (2007) and classified as daphnites. New analyses were carried out on these Fe-chlorites in order to perform geothermometric calculations. The Fe-chlorites were characterized by a high total octahedral occupancy (> 11.8) pointing to their trioctahedral component, high Fe^{2+} (a.p.f.u.) between 7.25 and 8.27, a varible Si (a.p.f.u.) content ranging from 4.9 to 5.4 and high Fe/(Fe+Mg) ratio between 0.84 and 0.88.

Chlorites from the altered rock of the top of the Olavarría Formation (<5 % vol.) were also characterized by a relatively high octahedral occupancy (11.9 - 11.7) and Fe/(Fe+Mg) ratio close to 0.8 (Table

TABLE 3a: Electron microprobe analyses of chlorite (Chl) from the altered Villa Mónica Fm. (VMFm) and Olavarría Fm. (OFm). Chlorites are based on 28. Fe* is either Fe^{2+} or Fe^{3+}. Temperature estimates are base on Zang and Fyfe (1995)'s equation (continue).

Mineral	Chl OFm					Chl VMFm											
Anal. nº	2	3	5	6	8	1	2	3	4	5	6	7	8	9	10	11	12
Samples	01181006					06181004											
SiO_2	24.31	25.28	25.84	24.53	24.67	21.84	23.08	23.38	23.06	22.82	22.90	21.52	23.72	23.29	22.03	22.72	24.34
TiO_2	0.05	0.05	0.04	0.03	0.03	0.01	0.01	0.03	0.01	0.00	0.00	0.02	0.02	0.01	0.01	0.02	0.02
Al_2O_3	18.71	18.32	18.52	18.67	18.93	20.83	21.31	21.03	20.41	21.09	21.26	21.69	21.08	21.00	21.04	20.70	21.37
FeO	39.97	38.02	38.32	38.81	38.75	42.89	41.72	41.45	41.53	41.88	41.94	43.40	41.47	42.53	41.65	43.15	42.79
MnO	0.00	0.00	0.00	0.01	0.00	0.11	0.25	0.15	0.15	0.23	0.17	0.12	0.13	0.19	0.20	0.13	0.20
MgO	5.30	6.17	5.83	6.20	5.51	3.31	3.58	3.54	3.55	3.65	3.78	3.45	3.70	3.33	3.35	3.64	3.51
BaO	0.02	0.00	0.00	0.00	0.02	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
CaO	0.04	0.08	0.11	0.06	0.12	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Na_2O	0.02	0.01	0.00	0.01	0.06	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
K_2O	0.16	0.28	0.28	0.15	0.30	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	**88.58**	**88.21**	**88.94**	**88.47**	**88.39**	**88.99**	**89.95**	**86.04**	**88.70**	**89.67**	**90.05**	**90.02**	**90.12**	**90.35**	**88.28**	**90.36**	**92.23**
Si	5.521	5.695	5.76	5.539	5.576	5.032	5.200	5.277	5.276	5.171	5.160	4.90	5.312	5.242	5.239	5.039	5.113
AlIV	2.479	2.305	2.236	2.461	2.424	2.968	2.800	2.723	2.724	2.829	2.840	3.100	2.688	2.758	2.761	2.961	2.887
AlVI	2.531	2.561	2.633	2.510	2.621	2.689	2.858	2.872	2.782	2.802	2.807	2.722	2.874	2.813	2.867	2.619	2.779
Ti	0.008	0.008	0.006	0.005	0.006	0.001	0.001	0.005	0.001	0.000	0.001	0.004	0.003	0.001	0.001	0.004	0.004
Fe^{2+}	7.593	7.163	7.150	7.329	7.327	8.264	7.860	7.824	7.948	7.936	7.905	8.266	7.766	8.005	7.905	8.253	8.052
Mn	0.000	0.000	0.000	0.001	0.000	0.021	0.048	0.029	0.030	0.044	0.032	0.023	0.024	0.037	0.038	0.025	0.037
Mg	1.794	2.072	1.938	2.088	1.855	1.137	1.202	1.191	1.211	1.231	1.271	1.170	1.236	1.116	1.134	1.241	1.177
Total VI	11.926	11.804	11.727	11.933	11.809	12.113	11.970	11.921	11.970	12.013	12.016	12.185	11.904	11.972	11.946	12.142	12.050
Ba	0.001	0.000	0.000	0.000	0.001	-	-	-	-	-	-	-	-	-	-	-	-
Ca	0.010	0.018	0.027	0.015	0.028	-	-	-	-	-	-	-	-	-	-	-	-
Na	0.008	0.003	0.001	0.002	0.027	-	-	-	-	-	-	-	-	-	-	-	-
K	0.047	0.081	0.082	0.044	0.086	-	-	-	-	-	-	-	-	-	-	-	-
Fe/(Fe+Mg)	0.809	0.776	0.787	0.778	0.798	0.879	0.867	0.868	0.868	0.866	0.861	0.876	0.863	0.878	0.875	0.869	0.872
T (ºC)	**242.5**	**248.7**	**255.3**	**243.1**	**253.1**	**252.7**	**271.7**	**273.2**	**263.6**	**266.0**	**266.9**	**256.5**	**273.9**	**266.0**	**272.0**	**246.2**	**262.9**

TABLE 3b: Electron microprobe analyses of chlorite (Chl) from the altered Villa Mónica Fm. (VMFm) and Olavarría Fm. (OFm). Chlorites are based on 28. Fe* is either Fe^{2+} or Fe^{3+}. Temperature estimates are base on Zang and Fyfe (1995)'s equation.

Mineral	Chl VMFm															
Anal. nº	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
Samples	06181004															
SiO_2	24.34	22.59	25.19	22.47	22.94	22.80	22.73	23.46	22.61	21.85	22.44	22.79	22.57	22.99	24.07	22.60
TiO_2	0.08	0.02	0.01	0.03	0.02	0.02	0.01	0.00	0.00	0.00	0.02	0.02	0.03	0.01	0.01	0.05
Al_2O_3	21.12	22.50	20.75	21.59	21.14	21.27	20.70	21.02	21.36	21.98	21.77	20.88	21.13	20.29	20.82	21.96
FeO	41.07	40.55	38.84	42.87	42.85	42.28	42.61	41.49	42.69	41.87	41.52	42.65	42.54	39.55	38.85	41.13
MnO	0.19	0.16	0.13	0.22	0.24	0.26	0.13	0.14	0.17	0.15	0.19	0.20	0.13	0.16	0.18	0.17
MgO	3.91	3.61	3.80	3.51	3.70	3.51	3.61	3.51	3.33	3.25	3.29	3.72	3.67	3.77	4.11	3.81
BaO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
CaO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Na_2O	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
K_2O	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	**90.71**	**89.43**	**88.72**	**90.69**	**90.89**	**90.14**	**89.79**	**89.62**	**90.16**	**89.10**	**89.23**	**90.26**	**90.07**	**86.77**	**88.04**	**89.72**
Si	5.389	5.084	5.628	5.057	5.145	5.146	5.166	5.292	5.109	4.992	5.100	5.149	5.109	5.320	5.430	5.080
AlIV	2.611	2.916	2.372	2.943	2.855	2.854	2.834	2.708	2.891	3.008	2.900	2.851	2.891	2.680	2.570	2.920
AlVI	2.899	3.052	3.092	2.783	2.734	2.806	2.712	2.881	2.798	2.912	2.932	2.710	2.747	2.760	2.920	2.910
Ti	0.013	0.004	0.001	0.005	0.003	0.003	0.002	0.000	0.000	0.000	0.003	0.004	0.004	0.000	0.000	0.000
Fe^{2+}	7.603	7.632	7.258	8.068	8.037	7.981	8.099	7.827	8.068	8.000	7.894	8.061	8.053	7.660	7.340	7.740
Mn	0.036	0.030	0.024	0.042	0.046	0.049	0.025	0.026	0.033	0.029	0.036	0.037	0.026	0.030	0.030	0.030
Mg	1.292	1.210	1.264	1.178	1.236	1.182	1.221	1.179	1.122	1.107	1.116	1.254	1.237	1.300	1.380	1.280
Total VI	11.843	11.928	11.639	12.075	12.057	12.021	12.059	11.913	12.022	12.048	11.981	12.066	12.068	11.75	11.67	11.96
Ba	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ca	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Na	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
K	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe/(Fe+Mg)	0.855	0.863	0.852	0.873	0.867	0.871	0.869	0.869	0.878	0.878	0.876	0.865	0.867	0.855	0.842	0.858
T (ºC)	**277.3**	**292.7**	**298.1**	**263.2**	**258.7**	**265.8**	**256.0**	**274.0**	**264.4**	**276.4**	**278.8**	**256.2**	**260.0**	**262.5**	**280.7**	**278.1**

TABLE 4: Kübler Index in hydrothermally altered basement (BAC 1-2) and Olavarría Fm. (OFm 1-2) rocks.

Sample	Grain fraction (μm)	Air dry Δ º2θ	Φ Δ º2θ	Degree	Glycolated ΦΔ º2θ	ΦΔ º2θ	Degree
BAC 1A	< 2	0.209	0.214	Epizone	0.210	0.209	Epizone
BAC 1B	< 2	0.218			0.208		
BAC 1A	< 0.2	0.199	0.203	Epizone	0.202	0.203	Epizone
BAC 1B	< 0.2	0.207			0.204		
BAC 2A	< 2	0.236	0.230	Epizone	0.236	0.236	Epizone
BAC 2B	< 2	0.223			0.235		
BAC 2A	< 0.2	0.221	0.218	Epizone	0.209	0.210	Epizone
BAC 2B	< 0.2	0.215			0.211		
OFm 1A	< 2	0.243	0.240	Anchi- to epizone	0.231	0.229	Epizone
OFm 1B	< 2	0.237			0.227		
OFm 1A	< 0.2	0.271	0.263	Upper anchizone	0.253	0.246	Upper anchizone
OFm 1B	< 0.2	0.254			0.238		
OFm 2A	< 2	0.327	0.335	Medium anchizone	0.242	0.245	Upper anchizone
OFm 2B	< 2	0.342			0.248		
OFm 2A	< 0.2	0.324	0.340	Medium anchizone	0.301	0.311	Medium anchizone
	< 0.2	0.356			0.321		

Limits diagenesis/anchizone is 0.600º - 0.400º and anchizone/ epizone is 0.240º - 0.010 Δº2θ.

TABLE 5: K/Ar mineral ages of different fine fractions of K-white mica of hydrothermally altered basement (BAC 1-2) and pyroclastic rock from top of the Olavarría Fm. (OFm 1-2) and Na-bearing alunite from the Las Águilas Fm.

Sample	Fine-fraction [μm]	K_2O [Wt%]	$^{40}Ar_{rad}$ [nl/g]	40Ar* [%]	Age [Ma]	2σ-Error Ma]
BAC 1	< 2	8.80	196.69	98.66	**586.5**	**7.0**
BAC 1	< 0.2	8.35	183.46	98.54	**578.0**	**8.1**
BAC 2	< 2	8.98	201.19	98.76	**587.7**	**6.2**
BAC 2	< 0.2	8.49	184.48	97.24	**572.5**	**6.9**
OFm 1	< 2	6.24	151.55	96.94	**629.4**	**8.2**
OFm 1	< 0.2	6.42	152.65	97.95	**618.2**	**10.9**
OFm 2	< 2	7.44	180.06	98.64	**627.5**	**10.2**
OFm 2	< 0.2	7.44	171.52	98.25	**602.2**	**13.2**
03161109	Alunite	5.95	177.85	98.50	**650.9**	**20.0**

3a). In the classification plot of Si (a.p.f.u.) vs. total Fe^{2+} (a.p.f.u.) chlorites fall within the ripidolite-brunsvigite upper limit with a daphnite tendency (Fig. 4c). Octahedral Al is higher than tetrahedral Al, whereas in the Fe-chlorites from base of the Villa Mónica this is undefined.

Al content in tetrahedral site of chlorites from both altered rocks was used as geothermometer (Table 3a-b) by applying the equation of Zang and Fyfe (1995). These authors introduced a correction factor into the equation of Cathelineau and Nieva (1985) considering the influence of Fe/(Fe+Mg) ratio > 0.34 in chlorites of hydrothermally altered bedrocks of the Igarapé Bahía gold deposit, Brazil. Such correction factor take into account the influence of the Fe/(Fe+Mg) ratio of the bulk composition over the chlorite chemistry. The obtained temperatures for the chlorites from the base of the Villa Mónica Formation and the altered pyroclastic rocks from the top of the Olavarría Formation range from 246 to 298ºC and 242 to 255ºC, respectively (Fig. 4d).

KÜBLER INDEX OF K-WHITE MICAS

The limits of Kübler Index values for diagenesis/anchizone and anchizone/epizone are 0.600º to 0.400º and 0.240º to 0.010 Δº2θ, respectively. X-ray diffractograms of altered BAC show that well-crystallized pure illite $2M_1$ constitute these samples (Fig. 6). KI values for these two samples are between 0.209-0.236 ± 0.005 Δº2θ (<2 μm fraction) and 0.203-0.218 ± 0.005 Δº2θ (<0.2 μm) (Table 4, Fig. 7), correlating with temperatures typical of the epizone (300-350°C). Samples of the Olavarría Formation have illite, quartz, little kaolinite and traces of feldpar. KI values of those illite of the altered pyroclastic rock from the Olavarría Formation (OFm 1-2) are in the range 0.229-0.335 ± 0.005 Δº2θ (<2 μm) and 0.246-0.340 ± 0.005 Δº2θ (<0.2 μm) (Table 4). They correlate with the medium anchizone until the transition to the epizone and then indicate lower temperatures (250-300°C) (Fig. 7). In fraction <2 μm, glycolated samples show a slight decreasement in the IK value, although no illite/smectite was recognized in these samples (Fig. 6).

K/AR DATING OF ALUNITE AND K-WHITE MICAS

Field observations reveal that alunite occurrence is much more restricted than mentioned by Zalba *et al.* (2007). Lenses of <7 cm wide and up to 25 cm long of a whitish clayey material (Fig. 3a) were found in the white claystones of the Las Águilas Formation from the western Barker quarries (Fig. 1). A sample composed of almost pure Na-bearing alunite was selected after identification of minerals by XRD and sent to Actlabs, Canada. The psedocubic alunite (Fig. 3b) has 5.95 wt. % of K_2O and gave an age of 650 ± 20 Ma (Table 5).

Four samples showing phyllitic alteration were collected from the altered migmatites of the basement (BAC 1 and 2) and the altered pyroclastic rock of the Olavarría Formation (OFm 1 and 2) underlying the micritic limestones of the Loma Negra Formation. As expected for almost pure fine-grained K-white micas, they show very high K_2O content, up to 9 wt. %, (Table 5). The four samples are thus considered suitable for determining the age of in-situ formed K-white micas.

Fine fractions of <2 μm and of <0.2 μm obtained from samples BAC 1 and 2 have ages ranging from 588 to 573 Ma. Samples OFm 1 and 2, following the same analytical procedure, show ages between 629 and 602 Ma. All age measurements yielded very high amounts of ^{40}Ar* (97-99%).

DISCUSSION

Constraints on temperatures of the hydrothermal fluids

The argillic alteration in the basement of east of Cuchilla de la Águilas (BAC 1 and 2) at the Tandilia Late-Proterozoic unconformity (TLPU), west of Barker, points to KI of epizonal realms for which derived temperatures are between ~300 - 350 °C. Assuming a geothermal gradient of 30 °Ckm^{-1} and a mean surface temperature of 20 °C estimated depths by overburden are between ~9.5 - 11 km. Geothermometry of chlorites of altered quartz arenites from the base of the Villa Mónica Formation at the TLPU in the cerro Chico hill (Fig. 1) indicates temperatures in the range of 246 - 298 °C (Fig. 3d and Table 3a-b). This range of temperatures approached the lower limit of the range of KI-derived temperatures determined in the argillic alteration of the basement. Furthermore, temperatures around 260 - 300 °C were estimated according to alteration mineral assemblages with pyrophyllite at the TLPU of Barker - Villa Cacique (Dristas *et al.* 2003, Dristas and Martínez 2007, Martínez and Dristas 2007). Less than 20 m above the TLPU, values of KI determined in diagenetic illite from the Villa Mónica Formation, Barker area, (Alló *et al.* 2000) indicated burial depths of <4 km, considering the same aforesaid geothermal gradient (Alló 2001). Likewise, Zalba *et al.* (2007) inferred that the sedimentary sequence of Tandilia has probably not exceeded 2 - 3 km of burial. The erosive unconformity at the top of the Villa Mónica Formation was useful for explaining differences in the thermal history of sedimentary units of the Sierras Bayas Group, unaffected by hydrothermal alteration, in the Olavarría area (Gómez Peral *et al.* 2011b). But in the Barker - Villa Cacique area the incongruence between the epizonal realms (>9.5 km) derived from the illite crystallinity of the altered basement (Fig. 7) and the <4 km depths reached on top of the Villa Mónica Formation, could be better explained by the formation of well-crystallized K-white micas (2M$_1$ polytype), where rocks at the TLPU were hydrothermally overprinted. Paleotemperatures of hydrothermal fluids derived from KI, of remarkably higher temperatures than those expected for diagenetic fluids, are supported by geothermometry of hydrothermal chlorite.

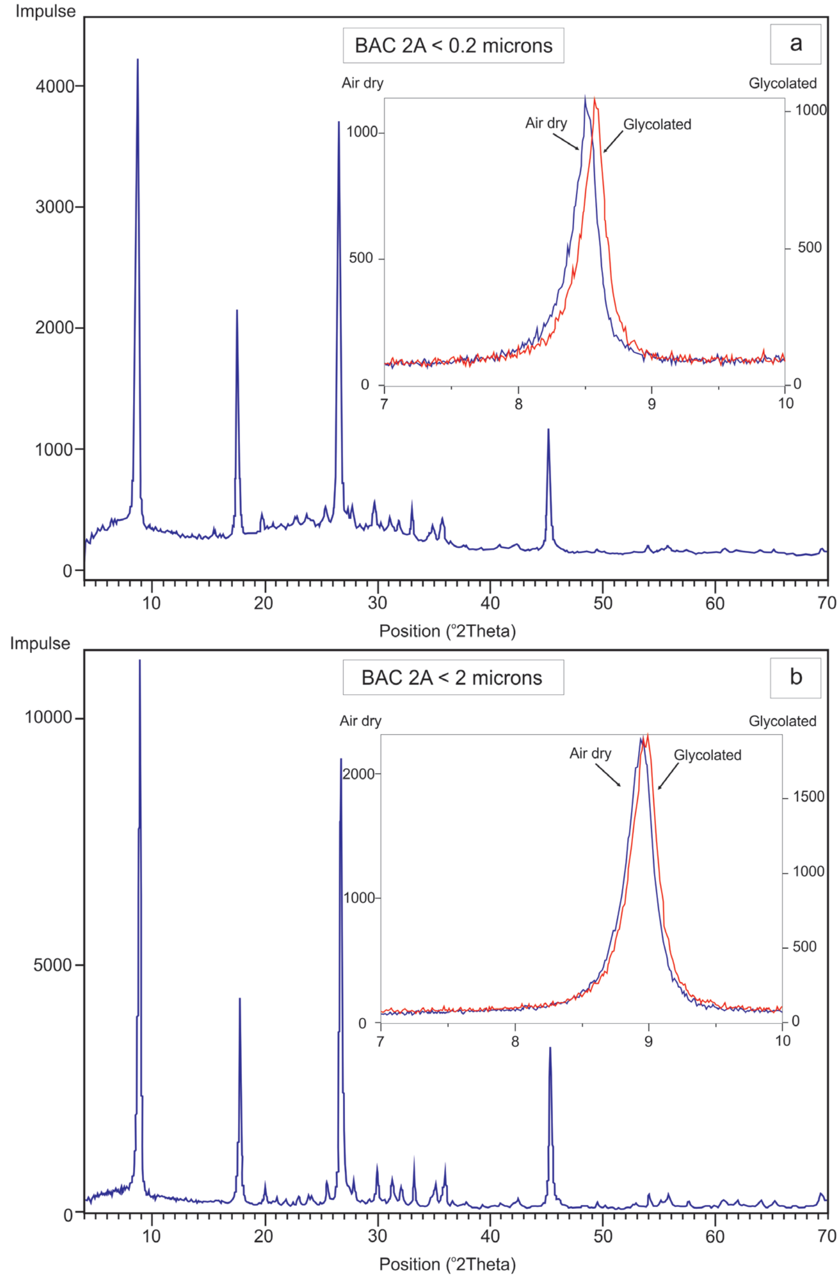

Figure 5: XRD patterns of oriented fine fractions of sample BAC 2 (duplicate A) with reflexion peaks of 2M1 illite and detail of the 001 reflexion peaks at air dry and glycolated conditions. a) Fraction < 0.2 µm b) Fraction < 2 µm.

At middle stratigraphic levels, in the massive microcrystalline quartz of the lower lithofacies of the Las Águilas Formation homogeneization temperatures measured on primary bi-phasic fluid inclusions were between 270 and 340°C (Dristas and Frisicale 1983) and on secondary fluid inclusion were between 120 - 150 °C (Dristas and Frisicale 1992). Besides, the first range of higher trapping temperatures is consistent with the min-

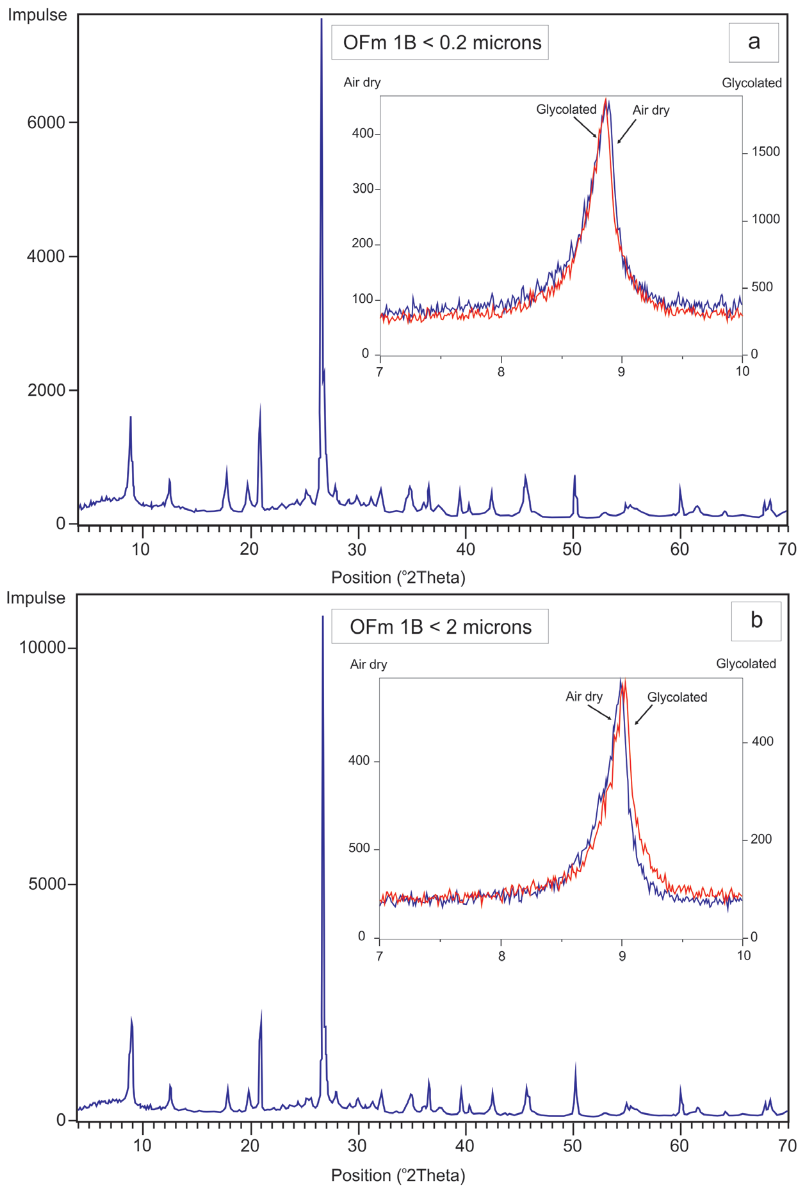

Figure 6: XRD patterns of oriented fine fractions of sample OFm 1 (duplicate B) with reflexion peaks of 2M1 illite and quartz and detail of the 001 reflexion peaks at air dry and glycolated conditions. a) Fraction < 0.2 µm b) Fraction < 2 µm.

eral assemblage of advanced argillic alteration (Dristas and Frisicale 1992). At higher levels, hot fluids interacted with relatively cooler host rocks and possibly with other cooler fluids, explaining why the KI values for K-white micas of the altered top of the Olavarría Formation are higher (lower crystalliniy) than those obtained in the BAC samples (Fig. 5). The lower limit of the range of temperatures derived from illite crystallinity (250 - 300 ºC) coincides with temperatures obtained by geothermometry on chlorites (242 - 255 ºC) present in the same altered pyroclastic rocks (Fig. 4d and Table 3a). Furthermore, microthermometry of fluid inclusion in altered rocks from the Barker area points to hydrothermal fluids with variable temperatures as low as ~100 ºC (Dristas and Frisicale 1992, Dristas and Martínez 2007, Martínez and Dristas 2007). The foregoing observations led us to hypothesize decreasing temperatures in the crystallization of the observed alteration mineral assemblages commonly in a stratigraphic upwards direction and/or after an input of hydrothermal fluids. Similarly, the formation of the hydrothermal clay mineral assemblages with pyrophyllite in the Olavarría area occurred at a relatively high temperature in the lower stratigraphic levels, Villa Mónica Formation, whereas temperatures in the realm of middle-deep mesodiagenesis (≤4 km and ≤120 ºC) were estimated for the Cerro Largo Formation (Gómez Peral *et al.* 2011a).

Age of the hydrothermal fluid flow

According to Dristas and Martínez (2007) the phyllic hydrothermal alteration of the basement rocks exposed in the western Barker area at the TLPU showed a bulk rock K/Ar age of 616 ± 17 Ma. This age is somewhat older than the ages of 588-573 Ma shown in the present work for illite fractions of the same highly altered migmatites (Table 5). A low scattering of the K/Ar ages around 600 Ma was also determined in K-white micas fine fractions from the hydrothermally altered pyroclastic (OFm 1 -2) underlying the black micritic limestone in the Loma Negra quarry, Villa Cacique (Table 5). Assuming an effective heating time of 10 ± 5 Ma, the total isotopic resetting of the <2 µm grain-size illite-muscovite fractions would be achieved at 260 ± 20 ºC (Hunziker *et al.* 1986). Hence, the ages obtained for the BAC samples may result from cooling after resetting of the K/Ar system by the hydrothermal overprint and its closure at ~ 260 ºC. Scatter shown by the ages of the BAC and OFm samples possibly resulted from incomplete isotopic resetting and/or the contribution from inherited older micas and K-feldspar (<5 % vol.), in the OFm samples. Consequently, the hydrothermal event must be younger than 629-618 Ma, or even 602 Ma. These two data sets delimit the age of the hydrothermal activity to *ca.* 620-590 Ma. The suggested time interval agrees with the K/Ar age obtained in pseudocubic Na-bearing alunites surveyed from the middle stratigraphic level, Las Águilas Formation (Table 5). Furthermore, the K/Ar ages of K-white micas from the Las Águilas Formation, associated with advanced argillic alteration (AAA) (Dristas and Frisicale 1983), cluster around 600 Ma (Bonhomme and Cingolani 1980). Dating of the thermal event calls for more detailed work, although similar ages (602 - 608 ± 18 Ma) were also obtained from well-crystallized K-white micas (Regalía 1987) from the hydrothermally altered sedimentary succession of San Manuel area (Dristas and Frisicale 1984), 50 kilometres southeast of Barker. All the aforementioned ages give geological support to the K/Ar age on alunite presented in this work and diverge from the obtained middle Permian (254 ± 7 Ma) K/Ar ages apparently for the same alunites from the Las Águilas Formation (Zalba *et al.* 2007). Hydrothermal mineral assemblages were also identified in the sedimentary succession of the Olavarría area (Poiré *et al.* 2005, Gómez Peral *et al.* 2011a, 2011b), but no ages were determined for this event affecting the Villa Mónica and Cerro Largo Formations. Therefore, Brasiliano ages of hydrothermal fluid flow determined in mineral assemblages with K-micas, alunite and pyrophyllite from the Barker area are of paramount importance in recognizing this thermal fluid-related event as unique, also affecting rocks of the Olavarría area.

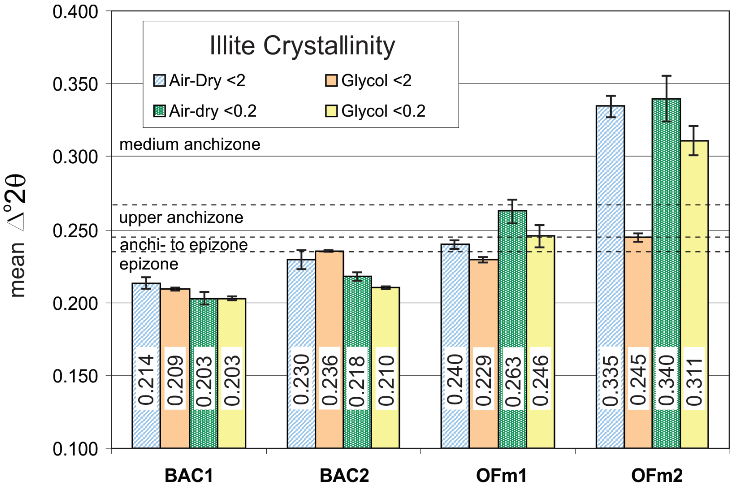

Figure 7: Mean illite crystallinity in hydrothermally altered basement (BAC 1-2) and Olavarría Fm. (OFm 1-2) rocks. Duplicates (A and B) of illite crystallinity are shown on top of each bar.

Possible source of the fluid flow

The above discussion raises the question of where the hydrothermal fluids came from. Two hypotheses could be argued: (1) the existence of hidden magmatic intrusions and/or (2) fluids derived from deep-seated metamorphic environments, i.e. fluids produced through prograde reactions. With respect to the second hypothesis, single pass flow (dominated by hydrostatic pressure and below ~ 6 km) in transition to a convective flow model (dominated by lithostatic pressure), more effective at shallower depths (Wood and Walther 1986), may explain an upwards fluid migration and interaction with basin rocks. Tectonic movements of the Brasiliano cycle (~600 Ma) produced vertical and horizontal displacements and led to an arrangement of blocks limited by the fault in the basement and in the sedimentary succession (Iñiguez-Rodriguez *et al.* 1989, Kostadinoff 1995). However, the consequences of a Brasiliano thermo-tectonic event at ~600 Ma has hitherto not been well constrained in the Tandilia belt. Anchizonal to epizonal meta-siltstones, meta-pelites and subordinated meta-sandstones of the Punta Mogotes Formation (Marchese and Di Paola 1975) (see table 1) gave four K-Ar ages, dating the last thermo-tectonic event between 576 ± 13 Ma and 615 ± 14 Ma (Cingolani and Bonhomme 1982). The Punta Mogotes Formation only exists in a drill core located near Mar del Plata (130 km SE of the Barker area) at the tip of the Tandilia belt (38° S) unconformably ~400 m below the Balcarce Formation (Marchese and Di Paola 1975). Detritial zircon U/Pb geochronology has been very useful not only for identifying sediment provenance sources but also for hypothesizing about sedimentation times. Regarding the Punta Mogotes Formation, Rapela *et al.* (2011) reported that this enigmatic unit portrays detrital zircons with U/Pb characteristic ages between 740-840 Ma among other older populations, which are absent from the Sierras Bayas Group and the Cerro Negro Formation. The lack of detrital zircon grains of Neoproterozoic ages in the Sierra Bayas Group and Cerro Negro Formation can be explained either by the absence of similar aged near positive source areas and/or by the absence of sedimentation during that time. Rapela *et al.* (2011) thus tentatively extrapolated the Sarandí del Yí shear zone and the Sierra Ballena shear zone observed in Uruguay and dated to be active at *ca.* 580 Ma (see Oyhançabal *et al.* 2011 and references therein). This eastern limit of the Tandilia belt against the proposed southward extension of the Dom Feliciano belt is referred to as Mar del Plata Terrane (Punta Mogotes Formation) (Rapela *et al.* 2011). As a result of the adjoining of this terrane at *ca.* 580 Ma, these authors argued that the Sierra Bayas Group and the Cerro Negro Formation must be older than Neoproterozoic, which is again inconsistent with the Ediacaran age (590-580 Ma) previously proposed by tentative chemostratigraphy for the upper Sierra Bayas Group (Gómez Peral *et al.* 2007). Our K/Ar radiometric ages on fine fractions of the uppermost section of the Olavarría Formation (upper Sierras Bayas Group) are in accordance with the latter hypothesis by which the entire sedimentary succession was already buried during the Late Neoproterozoic (Ediacaran).

CONCLUSIONS

Our K/Ar mineral ages in fine fractions of K-white micas from hydrothermally altered rocks and Na-bearing alunite, together with previous radiometric data, suggest that the hydrothermal event happened between 590 and 620 Ma, after the diagenetic overprint of the sedimentary pile. Illite crystallinity point to fluid temperatures in the range of 300-350 ºC for altered BAC rocks at the TLPU and temperatures of 250-300 ºC for the pyroclastic rocks of the Olavarría Formation. Chlorite geothermometry for both altered zones suggested lowers temperatures, 246 to 298 ºC for altered sandstone of the Villa Mónica Formation at the TLPU and 242 to 255 ºC for the Olavarría Formation. Folds, breccias and faults favored hydrothermal fluid migration and led to interaction with cooler host rocks and meteoric fluids at relatively shallower depths. Reactive rocks were easily overprinted by this fluid-related thermal event.

Temperatures of the hydrothermal event derived from illite crystallinity and chlorite geothermometry suggest depths unexpected for diagenesis of the sedimentary sequence. Thus, we proposed that deep-seated hydrothermal fluids would initially migrated from metamorphic realms in transition from lithostatic to hydrostatic pressure (simple pass-flow to convective flow). The broadly penecontemporaneous metamorphism of the Punta Mogotes Formation at *ca.* 600 Ma (Brasiliano orogeny), together with the possible contribution of heat from hidden igneous sources, provides a plausible origin for the hot fluids.

ACKNOWLEDGEMNTS

We are grateful to the Agencia Nacional de Promoción Científica y Tecnológica (ANPCYT) (J.A.D., PICT 2006/246) and to the Alexander von Humboldt Foundation (H-J.M., 3.4 -Fokoop_ARG/1005880). The authors are also indebted to the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and Universidad Nacional del Sur of Argentina (UNS) for providing stipends and research materials and to the Deutscher Akademischer Austauschdienst (DAAD) for granting a short-stay fellowship at the Institut für Mineralogie und Kristallchemie, Universität Stuttgart, to J.C.M. The author are also indebted to the companies Loma Negra C.I.A.S.A and Rothenberger S.C.A for their hospitality at the working area. Finally, the authors thank to the critical and constructive comments on the manuscript done by Dr. Gilda Collo and an anonymous peer-reviewer.

WORKS CITED IN TEXT

Alló, W.A. 2001. Los yacimientos de arcillas illíticas ferruginosas La Siempre Verde y La Placeres. Ph.D. Thesis, Universidad Nacional del Sur (unpublished), 235 p., Bahía Blanca, Argentina.

Alló, W.A., Domínguez, E.A. and Cravero, F. 2000. Calidad de las arcillas precámbricas de las facies silicoclásticas de la Formación Villa Mónica en el área de Barker, provincia de Buenos Aires, Argentina. 2º Congreso Latinoamericano de Sedimentología y 8º Reunión Argentina de Sedimentología: 30-31, Mar del Plata.

Andreis, R.R., Zalba, P.E., Iñiguez-Rodriguez A.M. and Morosi, M. 1996. Estratigrafía y evolución paleoambiental de la sucesión superior de la Formación Cerro Largo, Sierras Bayas (Buenos Aires, Argentina). VI Reunión Argentina de Sedimentología, actas: 293-298.

Árkai, P., Livi, K.J.T. and Horváth, P. 2003. Dioctahedral mixed K-Na-mica and paragonite in diagenetic to low-temperature metamorphic terrains: bulk rock chemical, thermodynamic and textural constraints. Central European Geology 51: 283-314.

Bonhome, M.G. and Cingolani, C.A. 1980. Mineralogía y geocronología Rb-Sr y K-Ar de fracciones finas de las Formación La Tinta, provincia de Buenos Aires. Revista de la Asociación Geológica Argentina 35: 519-538.

Cathelineau, M. 1988. Cation site occupancy in chlorites and illites as a function of temperature. Clay Minerals 23: 471-485.

Cathelineau, M. and Nieva, D. 1985. A chlorite solid solution geothermometer, The Los Azufres (Mexico) geothermal system. Contributions to Mineralogy and Petrology 91: 235-244.

Cingolani, C.A. 2011. The Tandilia System of Argentina as a southern extension of the Río de la Plata craton: an overview. International Journal of Earth Sciences (Geologische Rundschau) 100: 221-242.

Cingolani, C.A. and Bonhomme, M.G. 1982. Geochronology of La Tinta Upper Proterozoic sedimentary rocks, Argentina. Precambrian Research 18: 119-122.

Cingolani, C.A. and Bonhomme, M.G. 1988. Resultados geocronológicos en niveles peliticos intercalados en las dolomías de Sierra Bayas (Grupo La Tinta), provincial de Buenos Aires. Segundas Jornadas Geológicas Bonaerenses, Actas: 283-289, Bahía Blanca.

Cingolani, C.A. and Dalla Salda, L. 2000. Buenos Aires cratonic region. In: Cordani U., Milani, E., Thomaz Filho, A., Campo, D. (eds) Tectonic evolution of South America. 31º international Geological Congress, 139-146 Río de Janeiro.

Cingolani, C.A., Rauscher, R. and Bonhomme, M. 1991. Grupo La Tinta (Precámbrico y Paleozoico inferior) provincia de Buenos Aires, República Argentina. Nuevos datos geocronológicos y micropaleontológicos en las sedimentitas de Villa Cacique, partido de Juárez. Revista Técnica de YPFB: 177-191.

Dalla Salda, L.H. and Iñiguez-Rodríguez, A.M. 1979. La Tinta, Precámbrico y Paleozoico de Buenos Aires. 7º Congreso Geológico Argentino, Actas, I: 539-550, Neuquén.

De Caritat, P., Hutcheon, I. and Walshe, J.L. 1993. Chlorite geothermometry: A review. Clays and Clay Minerals 41: 219-239.

Dristas, J.A. and Frisicale, M.C. 1983. Presencia de alunita sódica y otras evidencias de alteración hidrotermal en el área ubicada al oeste de Barker, Sierras Septentrionales de la prov. de Bs. As. Revista de la Asociación Argentina de Mineralogía, Petrología y Sedimentología: 34-47.

Dristas, J.A and Frisicale, C.M. 1984. Estudio del yacimiento de arcillas del Cerro Reconquista, San Manuel, Sierras Septentrionales de Buenos Aires. 9º Congreso Geológico Argentino, Actas 5: 507-521, Buenos Aires.

Dristas, J. A. and Frisicale, M.C. 1987. Rocas piroclásticas en el sector suroeste de las Sierras Septentrionales de la prov. de Bs. As. Revista de la Asociación Argentina de Mineralogía, Petrología y Sedimentología 18: 46-53.

Dristas, J.A. and Frisicale, M. C. 1992. Breccias associated with hydrothermal clay deposits, Barker, Tandilia, Bs. As. Argentina. Zentralblatt für Geologie und Paläontologie Teil I,

H. 6 1901-1915.

Dristas, J.A. and Martínez, J.C. 2007. Late Proterozoic unconformity-related hydrothermal iron deposits in northern Barker area (Tandilia ranges, Argentina). Neues Jahrbuch für Geologie und Paläontologie, Abhandlungen 246: 267 - 281.

Dristas, J.A., Frisicale, M.C., and Martínez, J.C. 2003. High REE APS minerals associated to advanced argillic alteration in Cerrito de la Cruz clay deposit, Barker, Buenos Aires province, Argentina. Göttingen Arbeiten Zur Geologie und Paläontologie 5: 1-6.

Eberl, D.D. 1993. Three zones for illite formation during burial diagenesis and metamorphism. Clays and Clay Minerals 41: 26-37.

Essene, E.J. and Peacor, D.R. 1995. Clay mineral thermometry - A critical perspective. Clays and Clay Minerals 43: 540-553.

Fernández, R.R., Tessone, M., Etcheverry, R., Echeveste, H., Coriale, N. and Caballé, M. 2010. Interpretación de la distribución de elementos de las Tierras Raras en el basamento alterado de la zona de San Manuel, Provincia de Buenos Aires. Revista de la Asociación Geológica Argentina 64: 216-230.

Frey, M. 1987. Very low-grade metamorphism of clastic sedimentary rocks. In Frey, M. (ed.) Low Temperature Metamorphism. Blackie.

Frisicale, M.C. and Dristas, J.A. 2000. Génesis de los niveles arcillosos de Sierra de la Tinta, Tandilia. Revista de la Asociación Geológica Argentina 55: 3-14.

Fuhrmann, U., Lippolt, H.J. and Hess, J.C. 1987. Examination of some proposed K-Ar standards: ^{40}Ar/^{39}Ar analyses and conventional K-Ar-Data. Chemical Geology, Isotope Geoscience Section 66, 41-51.

Gómez Peral, L.E. 2008. Petrología y diagénesis de las unidades sedimentarias precámbricas de Olavarría, Provincia de Buenos Aires. Ph.D. Thesis, Facultad de Ciencias Naturales y Museo, Universidad Nacional de La Plata (unpublished), Part I: 327p. and Part II: 292 p., La Plata, Argentina.

Gómez Peral, L.E., Poiré, D.G., Strauss, H. and Zimmermann, U. 2007. Chemostratigraphy and diagenetic constraints on Neoproterozoic carbonate successions from the Sierras Bayas Group, Tandilia System, Argentina. Chemical Geology 237: 109-128.

Gómez Peral, L.E., Raigemborn, M.S., Ganem, F., Poiré, D.G. and Canalicchio, J.M. 2011a. Argilofacies con pirofilita en el Grupo Sierras Bayas, area de Olavarría, Argentina: Implicancias genéticas. 18º Congreso Argentino de Geología, Actas: 1100-1101, Neuquén.

Gómez Peral, L.E., Raigemborn, M.S. and Poiré, D.G. 2011b. Petrología y evolución de las facies silicoclásticas del grupo Sierras Bayas, Sistema de Tandilia, Argentina. Latin American Journal of Sedimentology and Basin Analysis 18: 3-14.

Gorokhov, L.M., Semikhatov, M.A., Baskakov, A.V., Kutyavin, E.P., Melnikov, N.N., Sochaya, A.V. and Turchenko, T.L. 1995. Sr isotopic composition in Riphean, Vendian, and Lower Cambrian Carbonates from Siberia. Stratigraphy and Geological Correlation 3:1-28.

Hartmann, L.A., Santos, J.O.S., Cingolani, C.A., McNaughton, N.J. 2002. Two Paleoproterozoic Orogenies in the Evolution of the Tandilia Belts, Buenos Aires, as evidenced by zircon U-Pb SHRIMP geochronology. International Geology Review 44: 528-543.

Heinrichs, H. and Herrmann, A.G. 1990. Praktikum der Analytischen. Geochemie, Springer Verlag, 669 p., Berlin.

Hillier, S., and Velde, B. 1991. Octahedral occupancy and the chemical composition of diagenetic (Low-Temperature) chlorites. Clay Minerals 26: 149-168.

Iacumin, M., Piccirillo, E.M., Girardi, V.A.V, Teixeira, W., Bellieni, G., Echeveste, H., Fernández, R., Pinese, J.P.P. and Ribot, A. 2001. Early Proterozoic calc-alkaline and middle Proterozoic tholeiitic dykes swarms from central-eastern Argentina: petrology, geochemistry, Sr-Nd isotopes and tectonic implication. Journal of Petrology 42: 2109-2143.

Inoue, A., Meunier, A., Patrier-Mas, P., Rigault, C., Beaufort, D. and Vieillard, P. 2009. Application of chemical geothermometry to low-temperature trioctahedral chlorites. Clay and Clay Minerals 57: 371-382.

Iñiguez-Rodriguez, A.M. and Zalba, P.E. 1974. Nuevo nivel de arcilitas en la zona de cerro Negro, Partido de Olavarría, provincial de Buenos Aires. Anales del LEMIT, Serie 2, 264: 95-100.

Iñiguez-Rodriguez, A.M., del Valle, A., Poiré, D., Spalletti, L. and Zalba, P.E. 1989. Cuenca Precámbrica/Paleozoica inferior de Tandilia, provincia de Buenos Aires. In: Chebli, G. and Spalletti, L. (eds) Cuencas Sedimentarias Argentinas. Universidad Nacional de Tucumán, Instituto Superior de Correlación Geológica, Serie de Correlación Geológica, 6: 245-263, Tucumán.

Jahren, J.S. and Aagaard, P. 1989. Compositional variations in diagenetic chlorites and illites, and relationships with formation-water chemistry. Clay Minerals 24: 157-170.

Ji, J. and Browne, P.R.L. 2000. Relationship between illite crystallinity and temperature in active geothermal systems of New Zealand. Clays and Clay Minerals 48: 139-144.

Jowett, E.C. 1991. Fitting iron and magnesium into the hydrothermal chlorite geothermometer. GAC/MAC/SEG Join Annual Meeting. Program with Abstract 16: A62, Toronto.

Kawashita, R. Varela, R. Cingolani, C. Soliani, E. Jr., Linares, E., Valencio, S.A., Ramos, A.M. and Do Campo, M. 1999. Geochronology and chemostratigraphy of "La Tinta" Neoproterozoic sedimentary rocks, Buenos Aires province, Argentina. 2º South American Symposium on Isotope Geology, 403-407, Córdoba.

Kisch, H.J. 1983. Mineralogy and petrology of burial diagenesis (burial metamorphism) and incipient metamorphism in clastic rocks. In Larsen G. and Chilingar, G.V. (eds.) Diagenesis in Sediments and Sedimentary Rocks 2. Elsevier, 289-493 p., Amsterdam.

Kostadinoff, J. 1995. Geofísica de las Sierras del Sistema de Tandil. Ph.D. Thesis, Facultad de Ciencias Astronómicas y Geofísicas, Universidad Nacional de La Plata (unpublished), 178p., La Plata.

Marchese, H.G. and Di Paola, E. 1975. Reinterpretación estratigráfica de la perforación Punta Mogotes Nº 1, provincia de Buenos Aires, Revista de la Asociación Geológica Argentina 30: 44-52.

Martínez, J.C. 2009. Estudio de la paleoactividad hidrotermal en el sureste de Tandilia, area de Barker-Villa Cacique. Ph.D. Thesis, Universidad Nacional del Sur (unpublished), 222 p., Bahía Blanca.

Martínez, J.C. and Dristas, J.A. 2007. Paleoactividad hidrotermal en la discordancia entre el Complejo Buenos Aires y la Formación La Tinta en el área de Barker, Tandilia. Revista de la Asociación Geológica Argentina 62: 375-386.

Martínez, J.C., Dristas, J.A., Massonne, H.J., and Theye, T. 2006. Alunite and REE rich APS minerals associated to the hydrothermal clay deposits in the Barker Area, Tandilia, Argentina. Clay Science 12: 15-20.

Martínez, J.C., Dristas, J.A., Massonne, H.-J. and Theye, T. 2010. A hydrothermal clay mineral assemblage at the Late Proterozoic unconformity in the Buenos Aires Complex - La Tinta Formation, Barker area, Tandilia Ranges (Argentina). Clays Minerals 45: 209-224.

Merriman R.J., and Frey M. 1999. Patterns of very low-grade metamorphism in metapelitic rocks. In Frey M, Robinson D. (eds) Low-grade metamorphism. Blackwell, 61-107 p., Oxford.

Morad, S., Ketzer, J.M. and De Ros, F.L. 2000. Spatial and temporal distribution of diagenetic alterations in siliciclastic rocks: implications for mass transfer in sedimentary basins. Sedimentology 47: 95-120.

Oyhançabal, P., Siegesmund, S., Wemmer, K. and Passchier, C.W. 2011. The transpresional connection between de Dom Feliciano and Kaoko Belts at 580-550 Ma. International Journal of Earth Sciences (Geologische Rundschau) 100: 379-390.

Poiré, D.G. 1993. Estratigrafía del Precámbrico sedimentario de Olavarría Sierras Bayas, provincial de Buenos Aires, Argentina. 13º Congreso Geológico Argentino y 3º Congreso de Exploración de Hidrocarburos, Actas 2: 1-11, Mendoza.

Poiré, D.G. and Spalletti, L.A. 2005. La cubierta sedimentaria Precámbrica - Paleozoica inferior del Sistema de Tandilia. In de Barrio, R.E., Etcheverry, R.O., Cabllé, M.F., Llambías, E. (eds) Geología y Recursos Minerales de la Provincia de Buenos Aires. 16º Congreso Geológico Argentino, Relatorio 4, 51-68, La Plata.

Poiré, D.G., Gómez Peral, L.E., Bertolino, S. and Canalicchio, J.M. 2005. Los Niveles con pirofilita de la Formación Villa Mónica, Precámbrico de Olavarría, Sistema de Tandilia, Argentina. 16º Congreso Geológico Argentino, Actas 2: 863-866, La Plata.

Rapela, C.W. Fanning, C.M., Casquet, C., Pankhurst, R. J., Spalletti, L., Poiré, D. and Baldo, E.G. 2011. The Río de la Plata craton and the adjoining Pan-African/brasiliano terranes: Their origins and incorporation into southwest Gondwana. Gondwana Research 20: 673-690.

Regalía, G. 1987. Carácteres Geológicos del area de San Manuel, Sierras Septentrionales de la provincia de Buenos Aires. Revista de la Asociación Geológica Argentina 42: 143-152.

Rieder, M., Cavazzini, G., D'Yakonov, Y.S., Frank- Kamenetskii, V.A., Gottardi, G., Guggenheim, S., Koval, P.V., Müller, G., Neiva, A.M.R., Radoslovich, E.W., Robert, J-L., Sassi, F.P., Takeda, H., Weiss, Z. and Wones, D.R. 1998. Nomenclature of the micas. Clays and Clay Minerals 46: 586-595.

Schumacher, E. 1975. Herstellung von 99,9997 % ^{38}Ar für die ^{40}K/^{40}Ar Geochronologie. Geochronologia Chimia 24: 441-442.

Steiger, R.H. and Jäger, E. 1977. Subcommission on Geochronology: Convention on the Use of Decay Constants in Geo- and Cosmochronology. Earth and Planetary Science Letters 36: 359-362.

Teixeira W., Pinese, J.P.P., Iacumin, M., Girardi, V.A.V., Piccirillo, E.M., Echeveste, H., Ribot, A., Fernández, R., Renne, P., and Heaman, L.M. 2002. Calc-alkaline and tholeiitic dyke swarms of Tandilia, Río de la Plata craton, Argentina: U-Pb, Sm-Nd and Rb-Sr ^{40}Ar-^{39}Ar data provide new clues for intraplate rifting shortly after Transamazonian orogeny. Precambrian Research 119: 329-353.

Velde, B. and Medhioub, M. 1988. Approach to chemical equilibrium in diagenetic chlorite. Contributions to Mineralogy and Petrology 98: 122-127.

Vidal, O. Parra, T. and Trotet, F. 2001. A thermodynamic model for Fe-Mg aluminous chlorite using data from phase equilibrium experiments and natural pelitic assemblages in the 100º to 600º C, 1 to 25 kb range. American Journal of Science 301: 557-592.

Warr, L.N. and Rice, A.H.N. 1994. Interlaboratory standardisation and calibration of clay mineral crystallinity and crystallite size data. Journal of Metamorphic Geology 12: 141-152.

Weaver, CE. and Broekstra, B.R. 1984. Illite-mica. In. Weaver C.E (ed.) Shale Slate Metamorphism in Southern Appalachians. Elsevier, 67-199 p., Amsterdam.

Wemmer, K. 1991. K/Ar- Altersdatierungsmöglichkeiten für retrograde Deformationsprozesse im spröden und duktilen Bereich - Beispiele aus der KTB-Vorbohrung (Oberpfalz) und dem Bereich der Insubrischen Linie (N-Italien). Göttinger Arbeiten zur Geologie und Paläontologie 51: 1-61.

Weber, K. 1972. Notes on the determination of illite crystallinity. Neues Jahrbuch für Mineralogie, Monatshefte 6: 267-276.

Winkler, H.G.F. 1974. Petrogenesis of metamorphic rocks. 3rd Edition. Springer-Verlag 320 p. New York.

Wood, B.J and Walther, J.V. 1986. Fluid flow during metamorphism and its implications for fluid-rock ratios. In Walther J.V. and Wood B.J., (ed.) Fluid-Rock Interactions During Metamorphism, Springer-Verlag 89-108 p. New York.

Worden, R.H. and Morad, S. 2003. Clay Minerals Cements in Sandstones. International Association of Sedimentologists, Special Publication 34.

Xiaofeng, L., Jingwen, M. and Renmin, H. 2005. A study of clay mineralogy and illite Kübler Index with respect to hydrothermal alteration in the Yinshan polymetallic deposit south China. Mineral Deposit Research: Meeting the Global Challenge, 4-24: 433-435.

Zalba, P.E., Andreis, R.R. and Lorenzo, F. 1982. Consideraciones estratigráficas y paleoambientales de la secuencia basal eopaleozoica en Cuchilla de las Águilas, Barker, Argentina. V Congreso Latinoamericano de Geología, Actas II: 389-409. Buenos Aires.

Zalba, P.E., Andreis, R.R. and Iñiguez-Rodriguez, A.M. 1988. Formación Las Águilas, Sierras Septentrionales de Buenos Aires, nueva propuesta estratigráfica. Revista de la Asociación Geológica Argentina 43: 198-209.

Zalba, P.E., Manassero, M., Laverret, E., Beaufort, D., Meunier, A. and Segovia, L. 2007. Middle Permian telodiagenetic processes in Neoproterozoic sequences, Tandilia System, Argentina. Journal of Sedimentary Research 77: 525-538.

Zang, W. and Fyfe, W.S. 1995. Chloritization of hydrothermally altered bedrock at the Igarapé Bahia gold deposit, Carajás, Brazil. Mineralium Deposita 30: 30-38.

Zimmermann, U., Poiré, D.G. and Gómez Peral, L. 2011. Neoproterozoic to Cover Palaeozoic successions of the Tandilia System in Argentina: implication for the palaeotectonic framework of southwest Gondawana. International Journal of Earth Sciences (Geologische Rundschau) 100: 489-510.

Recibido: 20 de diciembre, 2012
Aceptado: 23 de mayo, 2013