



## New insights into the Permian-Triassic magmatism of southern Cerro Cacheuta, Argentina

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### ABSTRACT

The igneous rocks of Cerro Cacheuta are considered a typical expression of the Permian-Triassic magmatism within the Andes Precordillera of Mendoza, Argentina. In particular, the southwestern margin of this hilltop is characterised by intermediate volcanic and felsic intrusives from the Choiyoi Group, one of the most extensive volcano-sedimentary suites of southern South America. The Choiyoi magmatism is widely associated with dramatic tectonic and environmental changes in the Gondwana supercontinent. Therefore, a better characterisation of the igneous facies of Cerro Cacheuta is critical to understand the evolution of Gondwana and recognise the multiple events that occurred towards the end of the Permian. This paper presents new data about the mineralogy, petrography, and geochemistry of the plutonic and volcanic units of Cerro Cacheuta, which enables authors to draw additional conclusions about the genesis and evolution of the magmatism in the region. Microscope observations indicate that the volcanic rocks are largely consistent with intermediate facies dominated by a porphyry texture with plagioclase and sanidine phenocrysts within a trachytic groundmass. Coetaneous breccias of possible hydrothermal origin and geodes with cryptocrystalline silica, limonite, and quartz are also recognised in outcrops. Geochemical analysis suggests that the lavas would likely correspond to andesites from a calc-alkaline magmatic arc. Furthermore, trace elements show enrichment in LREE/HREE, a slight negative anomaly in Eu, and concentration ratios compatible with crustal extension during the initial stages of the Choiyoi Group. Based on their chemical similarities, the monzonites of the Boca del Río Pluton would correlate with the lower section of the Choiyoi Group, of Permian age. In contrast, granites of the Cacheuta Pluton show a signature typically recognised in units from the Triassic and, therefore, would be comparable to the upper member of the Choiyoi Group.

*Keywords: mineralogy; petrography; geochemistry; Cerro Cacheuta; Argentina*

## Avances en el conocimiento del magmatismo Permo-Triásico del flanco sur del Cerro Cacheuta, Argentina

### RESUMEN

Las rocas ígneas del Cerro Cacheuta son consideradas una de las manifestaciones más típicas del magmatismo Permo-Triásico de la Precordillera de los Andes de Mendoza, Argentina. En especial, el flanco sudoeste del Cerro Cacheuta se caracteriza por la presencia de rocas volcánicas de composición intermedia e intrusivos felsicos del Grupo Choiyoi, una de las secuencias volcánico-sedimentarias de mayor distribución geográfica en Sudamérica. A su vez, el magmatismo del Choiyoi se asocia con los dramáticos cambios tectónico-ambientales que ocurrieron durante la ruptura del Gondwana. Es así que una caracterización más detallada de las facies ígneas del Cerro Cacheuta es clave para comprender tanto la evolución de Gondwana como los diferentes eventos que tuvieron lugar hacia fines del Pérmico. Este trabajo presenta nuevos datos sobre la mineralogía, petrografía y geoquímica de las rocas plutónicas y volcánicas del Cerro Cacheuta, con el objeto de lograr una interpretación más acabada de la génesis y evolución del magmatismo en la región. Al microscopio, las rocas volcánicas son consistentes con facies intermedias de textura predominantemente porfírica, con cristales de plagioclasas y sanidina en una pasta de composición traquítica. En afloramientos, también se han observado brechas posiblemente de origen hidrotermal, y geodas con sílice criptocristalina, limonita y cuarzo. Los resultados geoquímicos sugieren que las lavas tendrían una composición andesítica de arco magmático calco-alkalino. Por otra parte, los elementos traza muestran enriquecimiento en LREE/HREE, una leve anomalía de Eu y concentraciones químicas compatibles con un ambiente tectónico extensional durante los estadios iniciales del Grupo Choiyoi. En base a sus similitudes químicas, las monzonitas del plutón Boca del Río se correlacionarían con la sección inferior del Grupo Choiyoi. Por el contrario, los granitos del plutón Cacheuta muestran características típicas de unidades triásicas, por lo cual serían comparables con el miembro superior del Grupo Choiyoi.

*Palabras clave: mineralogía; petrografía; geoquímica; Cerro Cacheuta; Argentina*

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## 1. Introduction

A particularly extensive magmatism occurred during Permian-Triassic times between 26° and 40° south latitude, on the continental margins of South America. Products of this magmatism are currently seen within the Pastos Blancos Group in northern Chile and throughout outcrops from the Cordillera del Viento to the south and the Andes Precordillera of Mendoza, San Juan, and La Rioja to the north. Further inland, isolated units such as the Chadileuvú Block in La Pampa and minor igneous exposures in San Luis and even Buenos Aires provinces suggest that the magmatic activity would have gradually migrated eastwards from the Late Paleozoic. This magmatism province is considered to be part of the Choiyoi Group, a major feature comprising volcanic and plutonic rocks developed over a time span of approximately 36 Ma (Rocher et al., 2015), extending for more than 900,000 km<sup>2</sup> across Argentina and Chile (Bastías Mercado et al., 2020). The Choiyoi Group is composed of an andesite to dacite section at the bottom, and an upper section mainly rhyolitic in composition (Llambias et al., 1993). Numerous conceptual models have been postulated over the years to explain the origin of magmatism (e.g., Rocha Campos, 2011; Martinez et al., 2020; Bastías Mercado et al., 2020; and many others). As stated by Gianni and Navarrete (2022), some hypotheses explain the development of the Choiyoi Group due to very slow convergence or halted subduction by slab break-off episodes (e.g., Fanning et al., 2011; García-Sansegundo et al., 2014). Others propose a continued subduction scenario associated with changes in slab dip (e.g., Riel et al., 2018). Some studies suggest a convergent setting at ca. 280 Ma that experienced a slab break-off event after ca. 260 Ma (e.g., Ramos et al., 2020), whilst other authors favoured a subduction-related setting for part or the totality of the Choiyoi magmatic province (e.g., López de Luchi et al., 2021). Geochemical data from the present work, albeit limited, suggests that the Choiyoi rocks would have originated in a calc-alkaline magmatic arc with late extensional characteristics. Silicic rocks would have formed in an extensional setting where basaltic magmas caused extensive crustal melting that inhibited the upward passage of the basalts (Kay et al., 1989). This event could then have occurred at the initial stages of the Gondwana breakup. In addition, the Paleozoic magmatism would also constitute the source for the pervasive ash fall deposits interlayered in coeval, retroarc, or intracontinental basins near plate margins (Rocha Campos et al., 2011; Sato et al., 2015).

Most studies were undertaken in areas where the Choiyoi Group has greater geographical expression, typically in what is known as the Frontal Cordillera of Mendoza and San Juan. Pioneering works of Zuber (1889) and Stappenbeck (1910) established the presence of granite, diorite, and melaphyres in Cerro Cacheuta. Later, Rossi (1947) argued that these rocks were mainly lamprophyre and granodiorites akin to a common calc-alkaline magma. Petrographic studies by Llano et al. (1985) provided further evidence of granite (i.e., Cacheuta Stock) and granodiorites (i.e., Boca del Río Stock) in the locality. In that regard, Varela et al. (1993) classified the plutonic rocks of Cerro Cacheuta as monzodiorites, monzonites, and monzogabbros derived from a hybrid mantle-continental crust, possibly related to a continental post-collisional relaxation. More recently, Martínez (2005), Giambiagi and Martínez (2008) and Martínez et al. (2020) indicated that the Choiyoi Group is composed of three distinct lithologic facies ranging from the Early Permian to Early Triassic, which become increasingly felsic upwards. However, these studies were largely constrained to the Frontal Cordillera of Mendoza. The southern sector of Cerro Cacheuta was described by Ramos et al. (2010) when the Cerro Tupungato geological sheet was produced. Subsequently, an analysis of the geochemical signature of monzonites in the eastern edge of the Cacheuta Pluton suggested an origin contemporaneous with the Permian-Triassic volcanic activity of the Choiyoi Group (Cingolani et al., 2012). This data correlates well with U/Pb geochronology in the lower section of the Choiyoi Group near the neighbour towns of Potrerillos and Uspallata, which indicated a Late Permian age of  $277 \pm 3$  Ma (Strazzere et al., 2016).

Notwithstanding the many studies available in the literature, the widespread distribution, heterogeneous lithology and complex structure of the Choiyoi Group means that its origin and evolution are still in discussion. Therefore, the present work aims to describe and better characterise the mineralogy, petrography, geochemistry, and macroscopic aspects of the Choiyoi Group volcanic rocks in the little explored flanks of southern Cerro Cacheuta, Mendoza. Geochemical data was also analysed in relation to the neighbours Boca del Río and Cacheuta Plutons, of the Mesozoic age. In this context, the

analysis results provide additional data into the tectonic environment in which the Choiyoi rocks developed and contribute to the reconstruction of the region's geological evolution.

## 2. Method and Materials

The study area comprises an area of approximately 40 km<sup>2</sup> on the southern flank of the Cerro Cacheuta, within the Andes Precordillera of Mendoza in western Argentina (Figure 1). Existing geological information, satellite images, and base maps (scale 1:20,000) were processed and analysed employing Google Earth and the QGIS platform. Four field campaigns were then conducted to carry out geological mapping, lithological descriptions, structural measurements, and sampling of representative rocks. Selected specimens were then used for the preparation of thin sections at the University of San Luis and examined under a Leica petrographic microscope. Three samples from the Choiyoi Group (i.e., Ch1, Ch5, Ch6) were selected for geochemical analysis. The samples were analysed by X-ray fluorescence and ICP/MS (inductively coupled plasma-mass spectrometry) at ALS Laboratory Group Mendoza, Argentina. Geochemical results were processed using GCDKit 4.1 (Janoušek et al., 2006). Even though it is always desirable to further increase the number of analysed rocks, the collected samples are considered representative of the lithological variations in an area of limited geographical extension. Cryptocrystalline silica was studied by scanning electron microscopy (SEM), semi-quantitative microanalysis with dispersive spectroscopy (EDS), and WDS quantitative measurements at the University of San Luis LABMEM (Electron Microscopy and Microanalysis Laboratory).

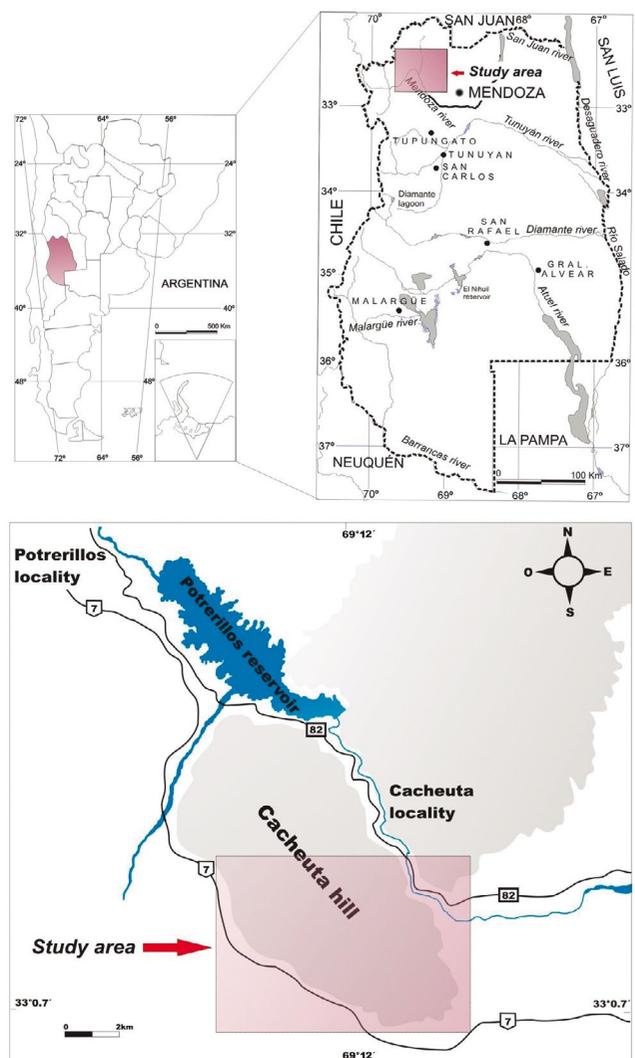


Figure 1. Location map of the study area.

### 3. Geological framework

#### 3.1 Tectonic setting and evolution

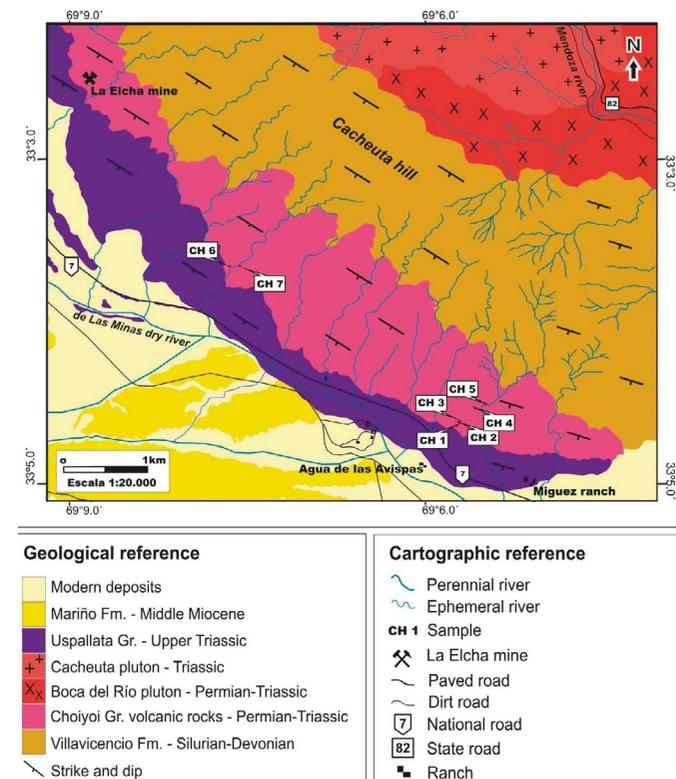
The Andes mountains extend for almost 8,000 km along the boundary between the Nazca and South American plates. The current morphology of the Andes is the result of a combination of pre-existing structures, deformation along the margins of Gondwana, and lithospheric shortening after the Cretaceous (Giambiagi et al., 2010). Following a series of compressive cycles in the Early Paleozoic, crustal extension became widespread during the Late Paleozoic – Mesozoic. Subduction would have commenced along the current continental margin during the Carboniferous (Ramos, 1988). Late Paleozoic deformation associated with the San Rafael orogenic phase occurred during the Late Permian (Azcuy and Caminos, 1987). The volcanic arc associated with subduction would be represented by Carboniferous – Permian plutonic and volcanic rocks currently outcropping in the Cordillera Frontal (Ramos et al., 1986; Mpodozis and Kay, 1990; Llambías et al., 1993). A change from compression to an extensional regime during the Late Permian to Middle Triassic led to important acidic volcanism and large volumes of magmatism under conditions of oblique extension (Llambías et al., 1993; Giambiagi and Martínez, 2008). Regional rifting further continued with the opening of the continental depocenters of Cacheuta and Las Peñas. Extension persisted from the Middle Triassic to the Late Cretaceous, although the deformation intensity and the affected areas varied considerably with time (Uliana et al., 1989). Moreover, the development of these rift systems would have been influenced by the reactivation of a weak crust along the edges of previously amalgamated terranes (Ramos et al., 1986). Compressive deformation during the Neogene–Quaternary resulted in the reactivation of Late Paleozoic faults favourably oriented with respect to the Andean stresses (Cortés et al., 1999; Folguera et al., 2004) and additionally, led to movements of the sinistral strike–slip faults from the Permian-Triassic (Cortés et al., 2006; Terrizzano et al., 2009). Thus, the Andes Precordillera of Mendoza is mostly characterised by some Ordovician carbonate platform sequences (Bordonaro et al., 1996), overlain by siliciclastic units and mafic rocks of the Lower Paleozoic, widespread sedimentites from the Devonian, granitic magmatism and extensive Permian–Triassic volcanism linked to the rupture of Gondwana (Llambías et al., 1993). Furthermore, continental paleoenvironments are developed due to Triassic rifting and ultimately, foreland basins filled with synorogenic deposits from the Paleogene.

#### 3.2 Stratigraphy

##### 3.2.1 Choiyoi Group Volcanics (Permian – Triassic)

Vulcanites of the Choiyoi Group were identified southwest of Cerro Cacheuta, usually in an array of near-horizontal banks with a general strike SW 25° (Figures 2; Figure 3a). The outcrops have grey–reddish tonalities due to the widespread presence of Fe oxides although, greenish types are usually more evident in hand specimens and fresh fractures (Figure 3b). These rocks are characterised by a porphyric texture with subhedral phenocrysts of plagioclase (1.5–4 cm in diameter), embedded in an aphanitic groundmass indicative of extrusive conditions. Phenocrysts of sanidine ranging between 1 to 3 cm and to a minor extent, angular lithics reaching up to 10 cm in length were also identified (Figure 3c). We also recognised minor and scattered outcrops of angular breccias, typically composed of large, multicolour volcanic fragments of several centimetres within a matrix of intermediate composition. The breccias generally exhibit a reddish coating, textural and mineralogical immaturity, and the presence of sub-angular polymictic clasts in a mafic matrix-supported fabric (Figure 3d). Thus, this volcanic breccia could be interpreted as a response to the opening of the conduits through which the lava escaped. Similarly, andesitic breccias were observed within the lowermost part of the Choiyoi Group further north, in proximities to the locality of Potrerillos (Martinez et al., 2020). Without direct radiometric measurements, the age of the volcanic rocks was inferred from regional correlations. In this context, compositionally similar lavas of the *Portezuelo del Cenizo Formation*, northwest of the study area near the locality of Uspallata, indicated an age of  $281 \pm 10$  Ma, from the Lower Permian (Folguera et al. 2004). This age agrees with previous results by Rapalini and Vilas (1991), who employed the K/Ar method in rocks of the same

formation further north, within *Quebrada del Tigre*. Further evidence of a Late Permian age was presented by Strazzere et al. (2016), who estimated an age of  $277 \pm 3$  Ma for the trachydacites and trachyandesites of the lower section of the Choiyoi Group. Thus, the trachyandesites observed in Cerro Cacheuta could be attributed to the beginning of the Choiyoi magmatism in the region.



**Figure 2.** Geological map of the southern sector of Cerro Cacheuta, Mendoza. Modified from Lara et al. (2017), Cingolani et al. (2012).



**Figure 3.** a) Overview of the Choiyoi Group volcanics on the western slope of Cerro Cacheuta, dipping towards the SW; b) volcanic rocks with grey-reddish tonalities due to Fe oxides coating; c) Porphyry texture with subhedral feldspar phenocrysts in an aphanitic matrix, together with angular volcanic lithics of a few centimeters randomly arranged. d) Breccia with a variety of lithics and clasts of the studied volcanic rocks.

### 3.2.2 Boca del Río Pluton (Late Permian)

The Boca del Río Pluton outcrops over about 25 km<sup>2</sup> in the NE portion of the study area. The granodiorite unconformably intrudes the greywackes and slates of the Villavicencio Formation. Rossi (1947) described it as the *Cacheuta Composite Stock*, originated from a granodiorite magma that was followed by a more extended pulse of granitic composition, named the Cacheuta Pluton. Metamorphic contact rocks such as hornfels occur around the edges of the stock due to temperature increases from the magma intrusion. In turn, the granodiorite is intruded by the Cacheuta Pluton, from the Triassic, as indicated by the dikes and aureoles adjacent to the contact between the units (Folguera et al., 2004). Rossi (1947) indicated that plagioclase, orthoclase, pyroxene, green amphibole, biotite and quartz are the primary minerals in the granodiorite. Accessories include mainly apatite, opaque minerals and titanite, along with secondary sericite and clays. Thus, and based on its mineralogical assemblage, the rock would better be classified as a quartz monzonite. Llano et al. (1985) argued that some rocks should still be considered granodiorites. Furthermore, Varela et al. (1993) distinguished three lithological types within the suite: quartz monzodiorites, quartz monzonites and monzogabbros. According to these authors, the monzodiorites are mostly composed of subeuhedral plagioclase (45 %), followed by crystals of anhedral quartz (20 %), hornblende (20 %) and perthitic orthoclase (15 %). Isolated flakes of biotite are occasionally observed. On the other hand, the monzonites are predominantly composed of plagioclase (40 %) and perthitic orthoclase (30 %), the later with signs of partial argillisation. Other minerals include aggregates of hornblende and biotite and accessories such as titanite, ilmenite, magnetite and zircon. Finally, the monzogabbros are characterised by augite-like and orthopyroxenes in association with subeuhedral Ca-plagioclases (50 %). The pyroxenes show some chlorite alteration near the edges whilst, signs of argillisation are identified around the plagioclases. Biotite, in this case associated to muscovite, is also present. Other accessories comprise mostly apatite and less titanite, ilmenite and magnetite (Varela et al., 1993).

Based on K/Ar dating on biotite, Caminos et al. (1979) reported and age of 397 ± 15 Ma (Lower Devonian) for the stock. Similar results were later recorded by Llambias et al. (1993) (418 ± 23 Ma; Lower Devonian) and Varela et al. (1993) using the Rb/Sr method (417 ± 35 Ma; Lower Devonian). Nevertheless, more recent studies by Cingolani et al. (2012) employing U/Pb on zircons from monzonites and monzogabbros yielded an age ranging between 261 ± 3.5 Ma and 255 ± 3 Ma, in the Late Permian.

### 3.2.3 Cacheuta Pluton (Middle to Upper Triassic)

The Cacheuta Pluton or Cerro Los Baños unit is a typical yellowish–pink granite that outcrops in the NE portion of the study area. This granite is a distinctive subvoid body intruding the already folded succession of clays and pelites of the Villavicencio Formation. The contact with the host rock is largely unconformable, with some hornfels product of the magmatism. Metasedimentary xenoliths of variable sizes are abundant across the granite and are attributed to fragments of country rock with minimal interaction with the ascending magma. In addition, a wide range of felsic and mafic dikes were found together in various sectors of the pluton, including its dome (Cingolani et al., 2012). Thin sections of the granite show widespread potassium feldspar, plagioclase, quartz and biotite with little muscovite. Allanite, apatite and magnetite were also recognised as accessories by Varela et al. (1993). In this regard, these authors classified the rock as a syenite granite.

Radiometric K/Ar by Dessanti and Caminos (1967) suggested that the granite emplacement occurred during the Late Permian (275 ± 13.5 Ma). In this regard, Varela et al. (1993) and Cingolani et al. (2021) indicated a <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.75105 for the granite, value compatible with a possible cortical source for the magma. Further north, analysis of K/Ar in the granites of Cerro Médanos and Cerro Arenal indicate an age of 244 ± 10 Ma (Middle Triassic) and 237 ± 10 Ma (Middle to Upper Triassic) respectively (Caminos et al., 1979). However, analysis of U/Pb on zircons from the monzonitic rim of Boca del Río defined a histogram with a main age mode between 253 – 258 Ma, in the Upper Permian (Cingolani et al. 2012). Thus, there is an ongoing discussion of the appropriate decay constant to be used and the radiometric age of the unit. Despite differences

in the proposed ages, the studies evidence that the emplacement of the Cacheuta Pluton took place during the Gondwanan cycle and would be coetaneous with the magmatic activity of the Choiyoi Group.

## 4. Results

### 4.1 Mineralogy and petrography

Microscope observations confirmed that the mineral primary assemblage of the Choiyoi vulcanites is plagioclase and sanidine in a pilotaxitic matrix (**Figure 4a-b**; **Table 1**). The subparallel orientation of the microliths of plagioclase evidence fluid circulation during the rock formation. In this regard, the matrix/phenocrysts ratio is estimated to be 70/30. The plagioclase is mostly subhedral, with blurred borders due to partial alteration to sericite and clays. Polysynthetic twinning has been occasionally identified in well-preserved phenocrysts. The composition of the plagioclase is intermediate. Sanidine, about 10 %, generally occurs in 1 – 2 cm grains, euhedral to subhedral in shape, Carlsbad twinned and ubiquitously cracked. Some grains are obscured by incipient alteration to clay with outer rims optically continuous suggesting thus, late crystalline growth. Isolated amphibole and biotite (5%) are present in the groundmass in association with apatite, titanite and less abundant opaque minerals (**Figure 4c-d**). The amphiboles are medium–grained, subhedral and greenish brown to reddish (**Figure 4e-f**). The biotite shows a typical long flaky habit, strong brownish coloration and potential changes of birefringence masked by the body colour. Finally, sparse grains of apatite, titanite and opaque minerals commonly occur in patches crossed by cracks and veinlets filled with chalcedony and jasper. Some fractures appear to be affected by recrystallisation and the inclusion of previously formed crystals. The rock matrix also shows zones highly stained by Fe oxides (**Figure 4g-h**).

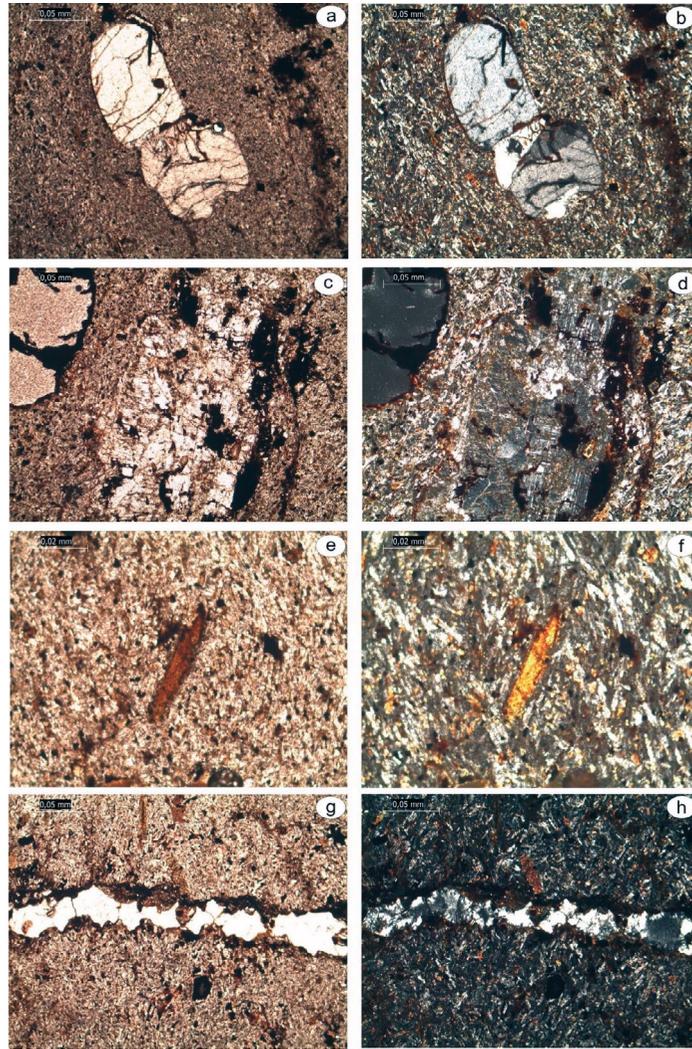
**Table 1.** Modal composition and whole-rock mineralogy of samples in southern Cerro Cacheuta.

	MAFIC LAVAS	Phenocrysts				Accessory minerals			Paste %	Secondary minerals			
		plagioclase	sanidine	amphiboles	biotite	apatite	titanite	opaques		sericite	clays	chalcedony	jasper
Choiyoi Group	Ch 1	15	10	5	5			x	65	*	*	*	*
	Ch 5	20	10	5		x	x	x	65	*	*	*	*
	Ch 6	20	10	5		x	x	x	65	*	*	*	*

Symbol X corresponds to accessory minerals (< 5%). Secondary minerals indicated by \*

As it will be discussed in more detail in the following sections, geochemical results indicate that the vulcanites in Cerro Cacheuta have a predominant trachyandesite composition.

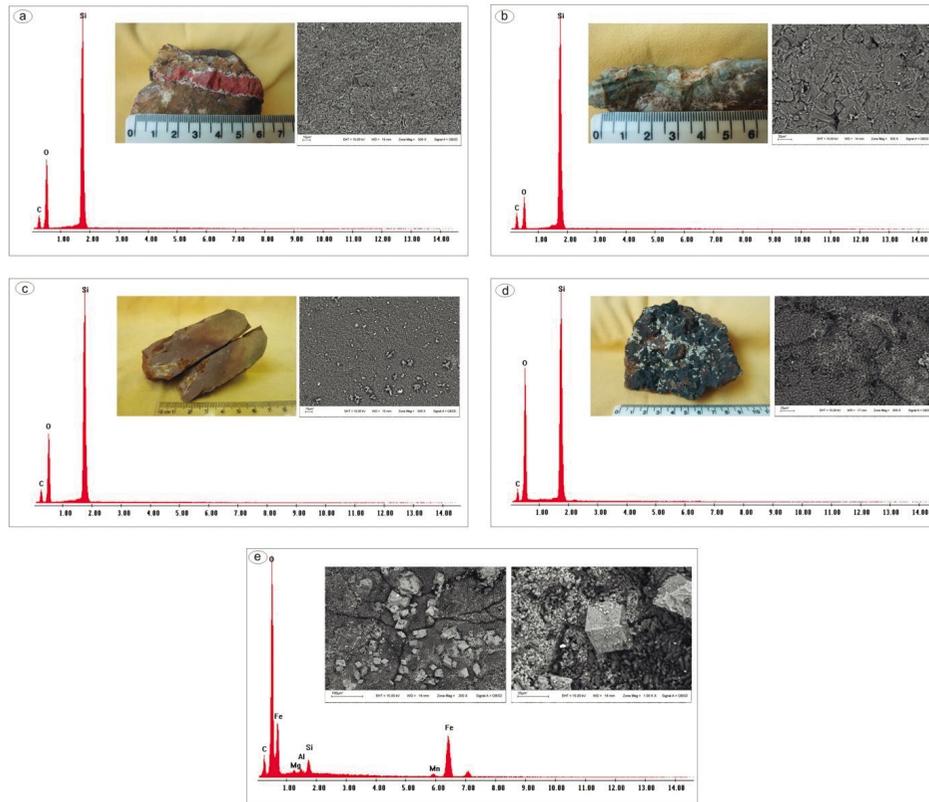
A puzzle-like type breccia was also observed in a few andesite outcrops (e.g., sample point Ch 7). These deposits are typically monomict and clast–supported, with angular clasts embedded in an aphanitic groundmass of cryptocrystalline silica, jasper and chalcedony. (**Figures 5a**). Cracks and veinlets are ubiquitous suggesting therefore, that the original texture have also been partially obliterated by hydrothermal alteration. Hydrothermal alteration in the lavas is also represented by numerous silica-bearing shear veins and patches of siliceous material in the wall rock. The alteration assemblage also shows lithic clasts commonly crossed by veinlets and infilled fractures, with a prevailing 315° azimuth direction and sinistral displacement (**Figure 5b**). The presence of geodes, commonly infilled by siliceous materials with classic comb or dog teeth texture is another indicator of extensive circulation of fluids (**Figures 5c**; **5d**). Thus, it is interpreted that the volcanic rocks would have been subjected to late hydrothermal processes contemporary with the development of the Permian–Triassic magmatism.



**Figure 4.** Microphotography of volcanic rocks of Choiyoi Group; a) Phenocrysts of subhedral sanidine slightly altered to clay, in a paste of plagioclase with pilotaxitic texture, 10X, N//; b) as in a) with crossed polarized, 10X, NX; c) Phenocrysts of subhedral plagioclase highly altered to clays and sericite. *Polysynthetic twinning* present in a few sections 10X, N//; d) as in c) with crossed nicols, 10X, NX; e) Phenocrystal of reddish brown amphibole in pilotaxitic paste, 10X, N//; f) the birefringence corresponding to the amphibole is masked by color, 10X, NX; g) Vein of chalcidony upholstered by jasper affecting the rock in a ductile manner, 10X, N//; h) as f) with crossed nicols, 10X, NX.



**Figure 5.** a) Puzzle-like breccia with clasts of lavas cemented by jasper-type materials, of possibly hydrothermal origin (sampling point Ch 7); b) jasper and chalcidony veins causing sinistral displacement of lithics; c) dog tooth geode filled with chalcidony and hyaline quartz; d) geode with euhedral crystals of purple amethyst quartz.



**Figure 6.** Siliceous material analysed by SEM-EDS: a) color orange; b) red; c) green; d) black with reddish stains; e) cubic, euhedral crystals. Peaks of higher intensity in the  $K\alpha$  Fe and  $K\alpha$  O possibly correlated with iron hydroxides from pyrite.

When analysed by electron microscope, the siliceous material reveals four contrasting colors: orange, red, green and black. The habit is quite variable, usually massive to botryoidal, diaphanous translucent, matt to oily gloss and of conchoidal fracture (**Figures 6a, b, c**). Individuals within the orange–red samples tend to be significantly smaller than green and black ones. In particular, some specimens exhibit reddish stains possibly due to the presence of limonites (**Figures 6d**). In addition, higher intensity in the  $K\alpha$  Fe and  $K\alpha$  O spectrum of cubic euhedral crystals can be associated to corrosion and limonitisation of Fe elements such as pyrite (**Figure 6e**).

#### 4.2 Geochemistry

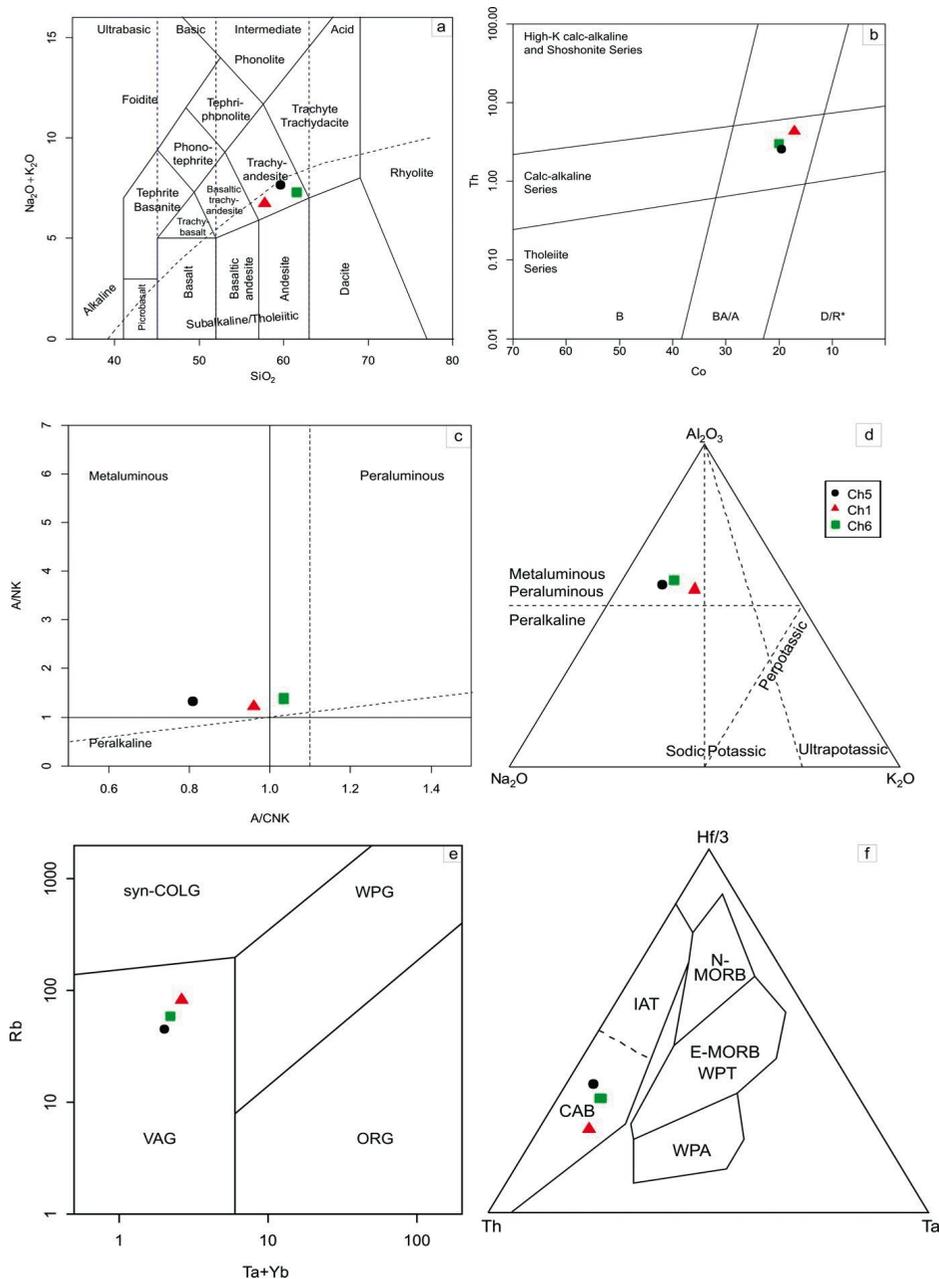
Bulk-rock chemistry for samples collected at Cerro Cacheuta is presented in **Appendix I**. The CIPW standard for samples *Ch5* and *Ch6* shows a predominantly quartz–hypersthene–diopside composition indicative of silica saturation. In turn, the normative composition of sample *Ch1* is quartz–hypersthene–corundum, reflecting then silica undersaturation, metaluminous and a slight peralkaline character (**Table 2**).

As previously discussed, the TAS  $\text{SiO}_2$  vs.  $\text{Na}_2\text{O}+\text{K}_2\text{O}$  classification (Le Bas et al. 1984), show samples plotting in the trachyandesite field (**Figure 7a**). A calc-alkaline trend is also suggested by the ternary AFM diagram (Irvine and Baragar, 1971). The immobile elements Th and Co (Hastie et al. 2007) are commonly employed as a proxy for  $\text{K}_2\text{O} - \text{SiO}_2$  in the identification of rock types and volcanic series. In this regard, the Th – Co classification diagram shows that samples plot on the calc-alkaline field (**Figure 7b**). Employing the diagram of Shand (1943) to discriminate according to alumina saturation, the Choyoi Group volcanic rocks show A/CNK values  $<1,1$  indicating thus a meta- and peraluminous character (**Figure 7c**). Any peraluminous signature is thought to be likely derived from metasedimentary sources (Collins and Richards, 2008), whilst the bulk of the rocks falling within the metaluminous field. This is

further confirmed by plotting results in the ternary diagram of  $\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{K}_2\text{O}$  (Foley et al. 1987; Shand, 1943). In this case, all samples plot well within the metaluminous and sodium field (**Figure 7d**). Pearce et al. (1984) proposed the use of incompatible elements to discriminate the tectonic environment. In this context, the Ta+Yb vs. Rb chart also shows that volcanic rocks from Cerro Cacheuta formed predominantly in a volcanic arc environment (**Figure 7e**). Concerning the tectonic framework, the Th–Hf–Ta diagram (Wood, 1980) points into a calc-alkaline arc within a destructive margin, heavily weighted into the Th-rich end (**Figure 7f**).

**Table 2.** CIPW-norm based on analyses recalculated to 100% on an anhydrous basis.

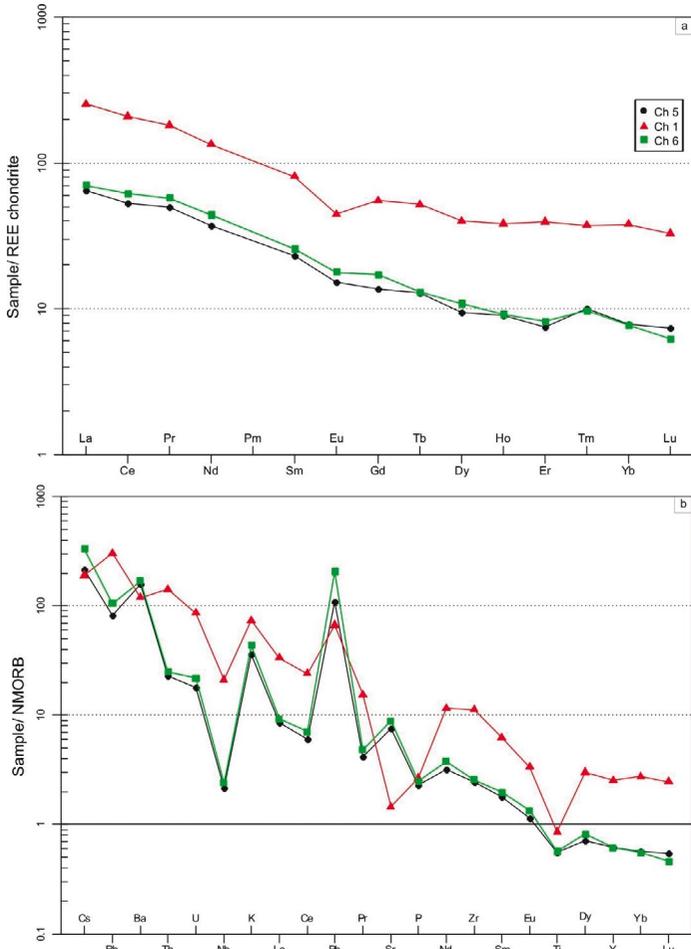
	Ch 5	Ch 6	Ch 1
Q	1.6	9.3	-
C	-	1.2	0.1
Or	15.3	18.6	31.3
Ab	43.8	38.7	35.3
An	9.7	8.2	8.1
Ne	-	-	1.1
Di	6.5	0.0	-
Hy	19.2	20.2	-
Ol	-	-	17.5
Mt	1.9	1.8	3.7
Il	1.3	1.4	2.1
Ap	0.6	0.7	0.7
Py	0.04	-	0.04
Sum	100.1	100.0	100.0



**Figure 7.** a) TAS diagram  $\text{SiO}_2$  vs.  $\text{Na}_2\text{O}+\text{K}_2\text{O}$  from Le Bas (1984); b) Co vs Th diagram de Hastie et al. (2007); c) A/CNK [ $\text{Al}_2\text{O}_3/(\text{CaO}+\text{Na}_2\text{O}+\text{K}_2\text{O})$ ] vs. A/NK [ $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O}+\text{K}_2\text{O})$ ] molecular relationship diagram (Shand, 1943); d) Ternary diagram of the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{K}_2\text{O}$  molar compositions (Foley et al., 1987; Shand, 1943); e) Ta+Yb vs. Rb diagram for granites classification from Pearce et al. (1984); f) Ternary diagram for classification of Th-Hf/3-Ta basalts from Wood (1980).

All samples are enriched in light rare earth elements (LREE) when analysed on chondrite-normalised REE (Nakamura, 1974) (Figure 8a). There are no significant differences in REE concentrations between samples *Ch5* and *Ch6*. However, sample *Ch1* exhibits lower  $\text{La}_N/\text{Yb}_N$  ratios and a higher enrichment in REE. A more pronounced Eu anomaly ( $\text{Eu}/\text{Eu}^*=0.66$ ), would indicate longer evolution and therefore, high chemical fractionation. Thus, a negative Eu anomaly would suggest plagioclase fractionation (Hanson, 1978). The vast majority of the LREE (La–Eu) would derive from feldspars, zircon, apatite, epidote and allanite whilst, HREE (Gd–Lu) contents could be related to pyroxene, amphiboles and especially, garnet. The general REEs pattern is compatible with a magma formed under a normal to thinned crust (~30 km) and indicative of plagioclase fractionation in a low-pressure environment (Kay et al.

1991). The NMORB (normal mid–ocean ridge basalt) multi-element diagram of Sun and McDonough (1989), shows negative anomalies in Rb, Nb, P and Ti. Simultaneously, these samples also present positive anomalies in Ba, K, Pb and Sr for samples *Ch5* and *Ch6* (Figure 8b). The positive anomaly in Pb but negative in Rb could reflect magma evolution in an arc system. On the other hand, a positive anomaly of Sr along with Eu is indicative of plagioclase fractionating in shallow levels of continental crust (Wilson, 1989). Sample *Ch1* is high in Rb but depleted in Sr. Concomitant positive anomalies in Th, U and Zr could indicate enrichment in the source or cortical fusion in a thinned continental crust (Green, 1980). Finally, higher contents in La and Ce at that sample could be attributed to a general increase in alkalinity while, negative anomalies in Ti may be associated to the fractionation of titanite.

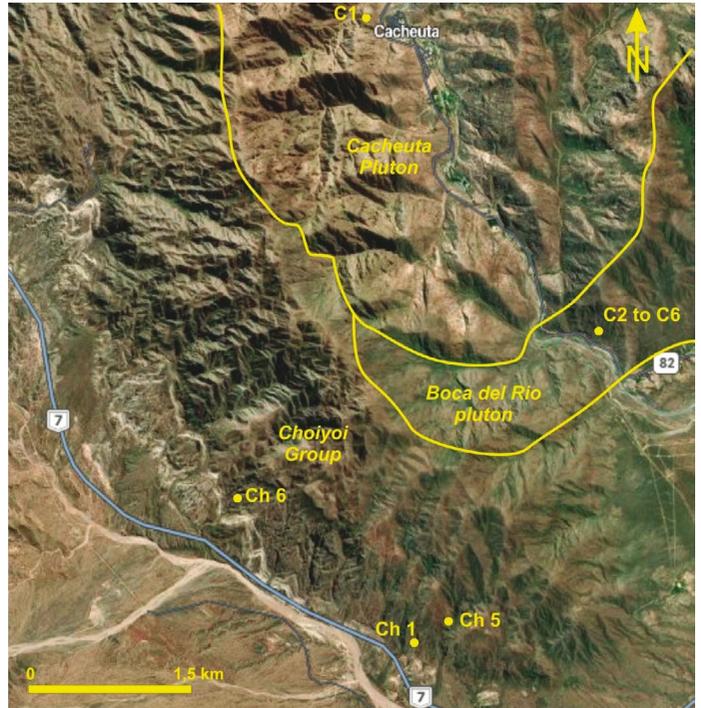


**Figure 8.** Volcanic rocks of the Choiyoi Group: a) rare earths elements (REE) normalised to chondrite from Nakamura (1974); b) minor elements and traces normalised to NMORB (Normal Mid-Ocean Ridge Basalt) from Sun and McDonough (1989).

## 5. Discussion

There are two main tectonic scenarios in which high-K calc-alkaline magmas may be generated: a) emplacement of high-K rocks in continental arc settings similar to that of the Andes (Pitcher, 1987), and b) melting and contamination spread of former continental crust in diverse tectonic settings (Roberts and Clemens, 1993). In this regard, samples from our study were compared with specimens C2 - C6 collected by Cingolani et al. (2012) from the Boca del Río Pluton, on the eastern margins of the Cacheuta Pluton, to further investigate any co-genetic relationships between units (**Figure 9**). Based on the  $\text{Na}_2\text{O}+\text{K}_2\text{O}$  vs  $\text{SiO}_2$  diagram from Middlemost (1994), samples C2 to C6 were classified as monzonites/quartz-monzonites, subalkaline, metaluminous and high - potassium. Sample C1, from the Cacheuta Pluton, indicates a granite composition (**Figure 10a**). Looking at the Th - Co classification diagram of Hastie et al. (2007), the samples plot into the high-K calc-alkaline field and shoshonites series, with increase in Co (**Figure 10b**). Specimens from both studies mostly cluster on the metaluminous field in the diagram  $\text{Al}_2\text{O}_3/\text{CaO}+\text{Na}_2\text{O}+\text{K}_2\text{O}$  (A/CNK) vs.  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}+\text{K}_2\text{O}$  (A/NK) of Shand (1943) (**Figure 10c**). Furthermore, the Th-Hf-Ta diagram (Wood, 1980) points into a tectonic framework characterised by a calc-alkaline arc within a destructive margin, heavily weighted into the Th-rich end (**Figure 10d**). While there is not sufficient evidence to completely rule out an arc signature due to inheritance/contamination, a closer look at minor and immobile elements further indicates that samples across sites are all consistent with a magmatic arc environment in the Nb/Yb vs. Th/Yb from Schandl and Gorton (2002), (**Figure 10e**). This is in

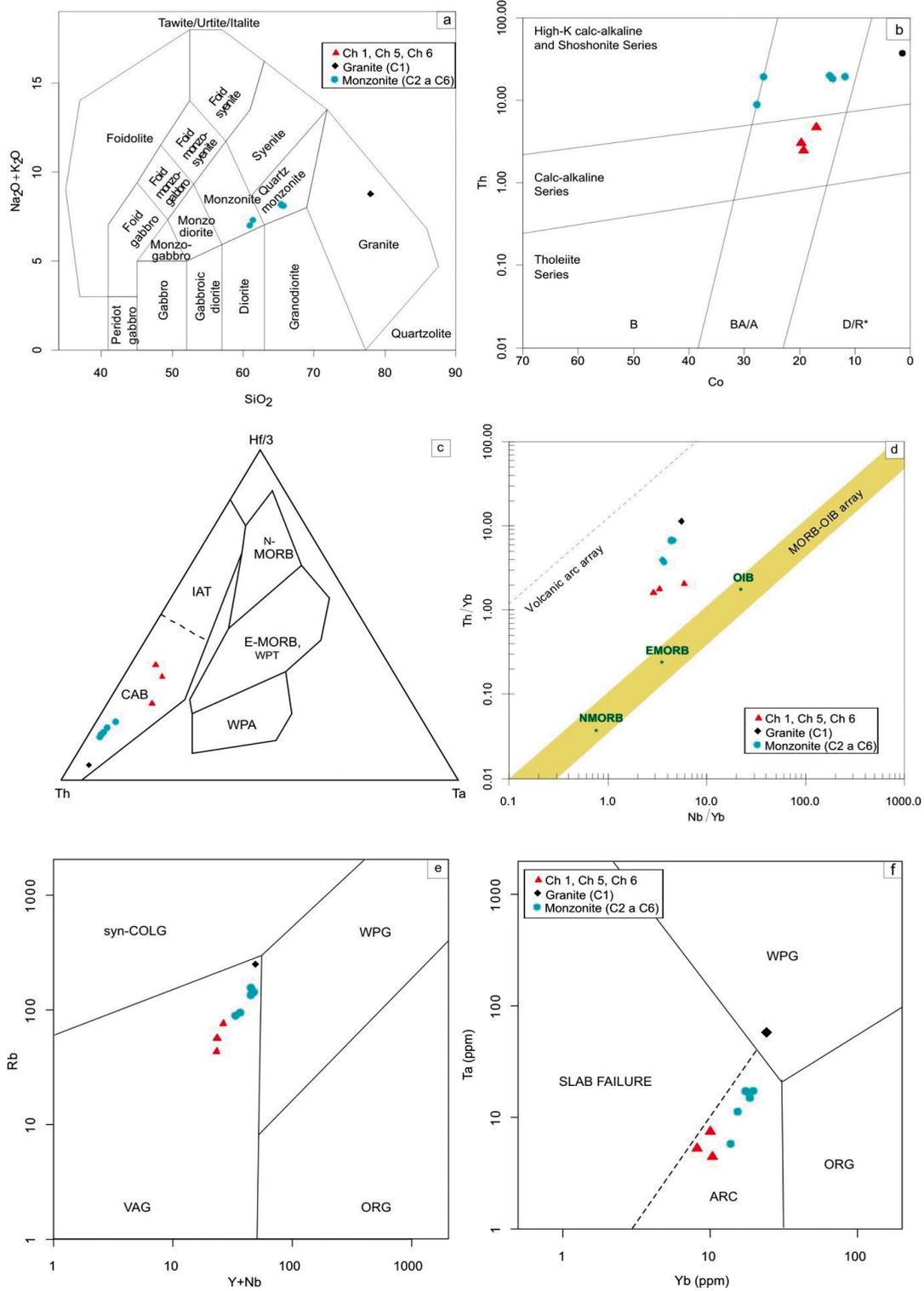
line with the transition from a volcanic arc to an intraplate setting as plotted in the Y+ Nb vs. Rb from Pearce et al. (1984). In addition, the Cacheuta samples mostly plotting in a tight group could also suggest formation in a single tectonic environment (**Figure 10f**).



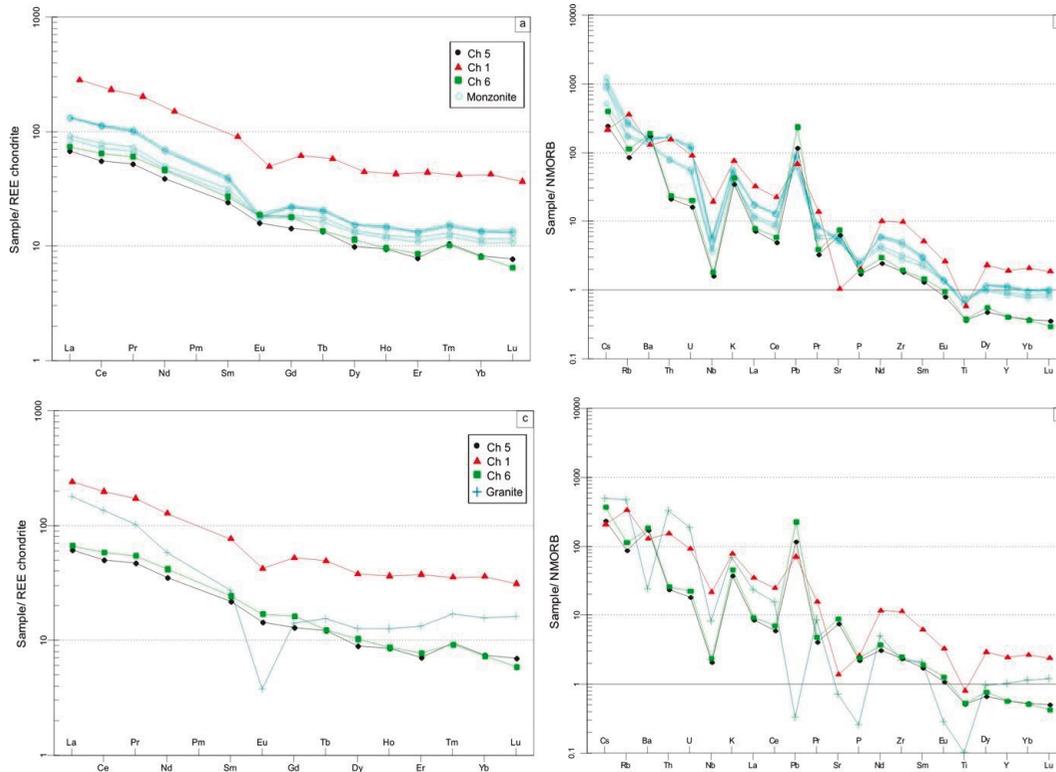
**Figure 9.** Location of the Ch1, Ch5 and Ch6 samples from the Choiyoi Group (present work). Samples C1 (Cacheuta Pluton) and C2 to C6 (Boca del Río Pluton) previously analysed by Cingolani et al. (2012).

With the exception of sample Ch1 which is enriched in REE, both monzonites (C2 to C6) and vulcanites (Ch5 and Ch6) display similar trends on a chondrite-normalised REE diagram (**Figure 11a**). On the other hand, samples C2 to C6 are enriched in LREE, with a near-flat trend in HREE and slightly negative anomaly of Eu. The observed negative anomaly in Eu suggests plagioclase fractionation at shallow depths (Hanson, 1978) whilst, the general pattern in REE would suggest rocks formation in a continental crust of normal thickness (~30 km) and plagioclase fractionation under low pressures. Normalising the elements to the NMORB diagram of Sun and McDonough, (1989) shows that the monzonites have positive anomalies in Cs, K, Pb, Sr, Nd but, negative in Rb, Nb, P and Ti (**Figure 11b**). Monzonitic rocks present a small variation in terms of their enrichment. Despite some variations in the magnitude of the negative anomalies for U and Th, these monzonites correlate well with samples Ch5 and Ch6 in the Choiyoi Group. On the other hand, sample Ch1 presents greater enrichment and therefore, positive anomalies in Rb and negative in Sr. The LILE elements (large ion lithophile elements) Rb and Ba, and the enrichment in K are all indicative of the fractionation of feldspars at low pressure, possibly due to cortical assimilation. Moreover, Pb enrichment might be associated with an arc signature. In contrast, and as stated by Hanson (1978), depletion of Sr and P could be attributed to the effects of sediments deposition. Anomalies of HFSE elements (high field strength elements) such as U and Th also indicate sedimentation or the effects of a crustal component. Finally, negative anomalies in Nb and Ti could be due to an arc component or associated to the fractionation of accessory minerals.

The granite of sample C1 exhibits similar trends to other units (**Figure 11c**). In this case, there is enrichment in LREE, with a near-flat trend in HREE and a strong negative anomaly of Eu. Again, the negative anomaly in Eu would suggest plagioclase fractionation under low pressures. However, the magnitude of the anomalies differs from other rocks when plotted on Spider diagrams. Thus, it is concluded that while there is a general good correlation between the monzonites and vulcanites, negative anomalies in Ba, Pb, P, Eu and Ti suggest that the granitic facies at Cerro Cacheuta are compositionally more variable (**Figure 11d**).



**Figure 10.** a) Diagram SiO<sub>2</sub> vs. Na<sub>2</sub>O+K<sub>2</sub>O from Middlemost (1994) for plutonic rocks, b) Co vs Th diagram de Hastie et al. (2007); c) Ternary diagram for classification of Th-Hf/3-Ta basalts, from Wood (1980); d) Nb/Yb vs. Th/Yb diagram from Schandl & Gorton (2002); e) Y+Nb vs. Rb diagram for granites classification, from Pearce et al. (1984), f) diagram Ta vs. Yb from Hildebrand et al. (2018), modified from Pearce et al. (1984). WPG–within plate granite; ORG–oceanic ridge granite.



**Figure 11.** Spider diagrams of the volcanic rocks of the Choiyoi Group (Ch1, Ch5 and Ch6) compared to monzonites from Boca del Río Pluton (C2 to C6): a) rare earths elements (REE) normalised to chondrite from Nakamura (1974); b) minor elements and traces normalised to NMORB (Normal Mid-Ocean Ridge Basalt) from Sun and McDonough (1989). Spider diagrams of the volcanic rocks of the Choiyoi Group (Ch1, Ch5 and Ch6) compared to Cacheuta pluton (C1): c) rare earths elements (REE) normalised to Nakamura's chondrite (1974); d) minor and trace elements normalised to NMORB (Normal Mid-Ocean Ridge Basalt) from Sun and McDonough (1989).

Martínez (2005) and Giambiagi and Martínez (2008) divided the magmatism of the Choiyoi Group into three major sections: a) a lower section of calc-alkaline composition, related to an environment of compressive subduction. This ultimately evolved into a magmatic arc that produced mafic rocks, basalts and andesites during the Permian; b) a middle section representing a transition towards greater extension, with rocks of more felsic compositions such as rhyodacites and dacites and: c) the upper section, with felsic rhyolites and granitic rocks originated within an extensional environment of alkaline characteristics. These rocks are linked to a temporary cessation of the subduction during the Triassic.

From this geodynamic context, it is then argued that rocks of trachyandesitic composition (i.e., CH1, Ch5 and Ch6) could be attributed to the lower section of the Choiyoi Group. In effect, these rocks not only have greater geological similarity with this section but are chemically closer to the Permian monzonites of C2 to C6, which based on trace element and REE patterns could in turn be considered the plutonic equivalent of those lava facies. On the other hand, the Triassic granitic pluton of C1 presents greater resemblance with the felsic, upper section of the Choiyoi Group, in this case associated to an extensional arc environment. According to Kay et al. (1991), its geochemical imprint suggest formation within a crust of normal thickness but already subject to extension.

## 6. Summary and conclusions

Findings from our study confirm that the vulcanites outcropping on the southwestern slopes of Cerro Cacheuta would correlate to trachyandesites from the Choiyoi Group, from the Permian – Triassic. At the microscope, the rocks typically consist of plagioclase and sanidine phenocrysts embedded in a groundmass of pilotaxitic texture. In outcrop, these rocks are characterised by numerous geodes and cavities, commonly coated with jasper and botryoidal chalcedony, or filled with quartz of dog-teeth and comb textures. Crystals of pyrite were also recognised. In many instances, the mineral is pseudomorphically replaced by iron hydroxides. Puzzle-like breccias and patches of bleached

clays might evidence hydrothermal processes following the lavas cooling. The geochemical signature of the rocks suggests that they formed at the transition between a calc-alkaline magmatic arc and an intraplate environment, with a slight tendency towards alkalinity. In turn, trace element exhibited some minor enrichment in LREE/HREE, a near-flat trend for HREEs and a slight negative anomaly in Eu in one of the samples. When normalised, the trace elements show a general negative anomaly in Rb, Nb, P and Ti and a positive anomaly for Ba, K, Pb and Sr. Thus, the trachyandesites are interpreted to be genetically related to a volcanic arc under a crust of average thickness. It is worthy to note that available data prevents us from entirely ruling out a crustal source, even though we do not support that model for the rocks under consideration. That implies that the transition from a calc-alkaline magmatism to a more alkaline and anorogenic one remains as a possible interpretation of the geodynamics of the region. In this case, the transition would simply reflect increasing extensional conditions during the emplacement of the Choiyoi Group.

The studied vulcanites were also compared to the coetaneous and nearby units of Boca del Río Pluton and the Cacheuta Pluton. In this case, geochemical data showed a close correspondence between the monzonites of Boca del Río pluton and the vulcanites of the Choiyoi Group. Nonetheless, the REEs signature of the trachyandesite/monzonites suggests that despite genetic similarities, rocks from Boca del Río could reflect greater petrological evolution and a more evolved magma. In this regard, the monzonites would correlate with igneous rocks at the lower section of Choiyoi Group, possibly of Late Permian age. These units were later affected by the intrusion of the Cacheuta Pluton, with the consequent thermal imprint in the host rocks.

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