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GEOLOGICAL NOTE

Early Cambrian U-Pb zircon age and Hf-isotope data from the Guasayán pluton, Sierras Pampeanas, Argentina: implications for the northwestern boundary of the Pampean arc

***Juan A. Dahlquist[1], Sebastián O. Verdecchia[1], Edgardo G. Baldo[1], Miguel A.S. Basei[2], Pablo H. Alasino[3, 4], Gimena A. Urán[5], Carlos W. Rapela[6], Mario da Costa Campos Neto[2], Priscila S. Zandomeni[1]**

[1] *CICTERRA-CONICET-UNC, Avda. Vélez Sarsfield 1611, Edificio CICTERRA, X5016CGA Córdoba, Argentina. jdahlquist@efn.uncor.edu; sverdecchia@gmail.com; ebaldo@efn.uncor.edu; priscilazandomeni@hotmail.com*
[2] *Instituto de Geociências da Universidade de São Paulo, Rua do Lago 562, 05508-080 São Paulo, SP, Brasil. baseimas@usp.br; camposnt@usp.br*
[3] *INGeReN-CENIIT-UNLaR, Avda. Gobernador Vernet y Apostol Felipe 5300, La Rioja, Argentina. phalasino@gmail.com*
[4] *CRILAR-CONICET, Entre Ríos y Mendoza 5301, Anillaco, La Rioja, Argentina.*
[5] *FCEFyN-UNC, Avda. Vélez Sarsfield 1611, X5016CGA Córdoba, Argentina. gimeuran@gmail.com*
[6] *CIG-CONICET-UNLP, Calle 1 N° 644, 1900 La Plata, Argentina. crapela@cig.museo.unlp.edu.ar*

** Corresponding author: jdahlquist@efn.uncor.edu*

ABSTRACT. An Early Cambrian pluton, known as the Guasayán pluton, has been identified in the central area of Sierra de Guasayán, northwestern Argentina. A U-Pb zircon Concordia age of 533±4 Ma was obtained by LA-MC-ICP-MS and represents the first report of robustly dated Early Cambrian magmatism for the northwestern Sierras Pampeanas. The pluton was emplaced in low-grade metasedimentary rocks and its magmatic assemblage consists of K-feldspar (phenocrysts)+plagioclase+quartz+biotite, with zircon, apatite, ilmenite, magnetite and monazite as accessory minerals. Geochemically, the granitic rock is a metaluminous subalkaline felsic granodiorite with SiO_2=69.24%, Na_2O+K_2O=7.08%, CaO=2.45%, Na_2O/K_2O=0.71 and FeO/MgO=3.58%. Rare earth element patterns show moderate slope (La_N/Yb_N=8.05) with a slightly negative Eu anomalies (Eu/Eu*=0.76). We report the first *in situ* Hf isotopes data (ε_{Hft}=-0.12 to -4.76) from crystallized zircons in the Early Cambrian granites of the Sierras Pampeanas, helping to constrain the magma source and enabling comparison with other Pampean granites. The Guasayán pluton might provide a link between Early Cambrian magmatism of the central Sierras Pampeanas and that of the Eastern Cordillera, contributing to define the western boundary of the Pampean paleo-arc.

Keywords: U-Pb Geochronology, Hf isotopes, Pampean granites, Sierra de Guasayán.

RESUMEN. Edad U-Pb y análisis isotópico de Hf en circones del plutón Guasayán del Cámbrico temprano, Sierras Pampeanas, Argentina: implicancias para el límite noroccidental del arco pampeano. Un plutón de edad Cámbrica temprana, conocido como plutón Guasayán, ha sido identificado en el área central de la sierra de Guasayán, noroeste de Argentina. Una edad U-Pb en concordia de 533±4 Ma fue obtenida en circones mediante LA-MC-ICP-MS. Esta edad representa el primer reporte de magmatismo Cámbrico temprano para el noroeste de las Sierras Pampeanas. El mismo está emplazado en rocas metasedimentarias de bajo grado y se caracteriza por una asociación magmática de K-feldespato (fenocristales)+plagioclasa+cuarzo+biotita, con circón, apatita, ilmenita, magnetita y monacita como minerales accesorios. Geoquímicamente, la roca granítica se clasifica como una granodiorita félsica metaluminosa subalcalina con contenidos de SiO_2=69,24%, Na_2O+K_2O=7,08%, CaO=2,45% y relaciones de Na_2O/ K_2O=0,71 y FeO/MgO=3,58%. Los patrones de elementos de tierras rara muestran una pendiente moderada (La_N/Yb_N=8,05) con una ligera anomalía negativa de Eu (Eu/Eu*=0,76). Nosotros reportamos los primeros datos *in situ* de isótopos de Hf (ε_{Hft}=-0,12 a -4,76) para circones cristalizados en granitos del Cámbrico temprano de Sierras Pampeanas, lo que aporta información crítica sobre la fuente de los magmas, permitiendo la comparación con otros granitos pampeanos. El plutón Guasayán podría proveer el enlace entre el magmatismo del Cámbrico temprano del sector central de las Sierras Pampeanas y aquel de la cordillera Oriental, contribuyendio a definir el límite occidental del paleoarco Pampeano.

Palabras clave: Geocronología U-Pb, Isótopos de Hf, Granitos pampeanos, Sierra de Guasayán.

1. Introduction

The Sierras Pampeanas were sub-divided into Western and Eastern sectors according to their dominant lithologies (Caminos, 1972) (Fig. 1), whereas modern geochronological studies demonstrate that they correspond to different geological histories, as summarized below.

The Western Sierras Pampeanas are dominated by 1030-1330 Ma (“Grenville orogen”) igneous and metamorphic rocks, intruded by relatively scarce Ordovician granites of the Famatinian cycle (*e.g.*, Casquet *et al*., 2001; Sato *et al*., 2003; Rapela *et al*., 2010; Varela *et al*., 2011 and references therein). The Eastern Sierras Pampeanas are characterized instead by a low- to high-grade Late Ediacaran to Early Palaeozoic basement, intruded by voluminous granitic batholiths and plutons of Early Cambrian (*Pampean*), Early Ordovician (*Famatinian*), Middle-Late Devonian (*Achalian*) and Carboniferous (*Early Gondwana*) age (see references cited in Dahlquist *et al*., 2014).

The oldest and best-studied unit of the Pampean basement is the Puncoviscana Formation (originally defined by Turner, 1960), a thick sequence (>2,000 m) formed by very low-grade marine metasedimentary succession, deposited in the Late Ediacaran (Omarini *et al*., 1999), but mainly in the Early Cambrian, and folded still within the Early Cambrian (537-523 Ma, Escayola *et al*., 2011 and references therein). Based mainly on ages from detrital zircons, the metasedimentary rocks of the Eastern Sierras Pampeanas are considered to be higher grade equivalents of this formation, more intensely affected by the Pampean orogeny (Toselli, 1990; Willner, 1990; Rapela *et al*., 1998; Schwartz and Gromet, 2004; Escayola *et al*., 2007; Rapela *et al*., 2007; von Gosen and Prozzi, 2009; Rapela *et al*., 2015 and references therein).

Early Cambrian magmatism recognized in the Eastern Cordillera and Eastern Sierras Pampeanas is known as Pampean magmatic arc (*e.g.*, Rapela *et al*., 1998; Omarini *et al*., 2008; Hauser *et al*., 2011; Iannizzotto *et al*., 2013; von Gosen *et al*., 2014 and references therein).

The metasedimentary rocks of Sierra Norte and Ambargasta are intruded by metaluminous and peraluminous granitic rocks of Early Cambrian age forming the Sierra Norte-Ambargasta batholith (Lira *et al*., 1997; Iannizzotto *et al*., 2013). The Early Cambrian Tastil batholith has two main intrusive phases, gray granodiorite and red granite. Extensive outcrops of a porphyry dacite are also associated with the intrusive rocks. In the southern part of the batholith the gray granodiorite intruded folded turbidites of the Neoproterozoic Puncoviscana Formation (Hauser *et al*., 2011). Studies of the Early Cambrian granites (541-530 Ma) of the Sierras Pampeanas and Eastern Cordillera indicate that crystallized from metaluminous calc-alkaline subduction-related magmas (*e.g.*, Hauser *et al*., 2011; Iannizzotto *et al*., 2013 and references therein). In Sierras Pampeanas, late peraluminous granites (530-520 Ma) were linked with a post-collisional event (*e.g.*, Rapela *et al*., 1998; Iannizzotto *et al*., 2013).

Located to the northwest of Sierra Norte-Ambargasta batholith, the Sierra de Guasayán (Beder,

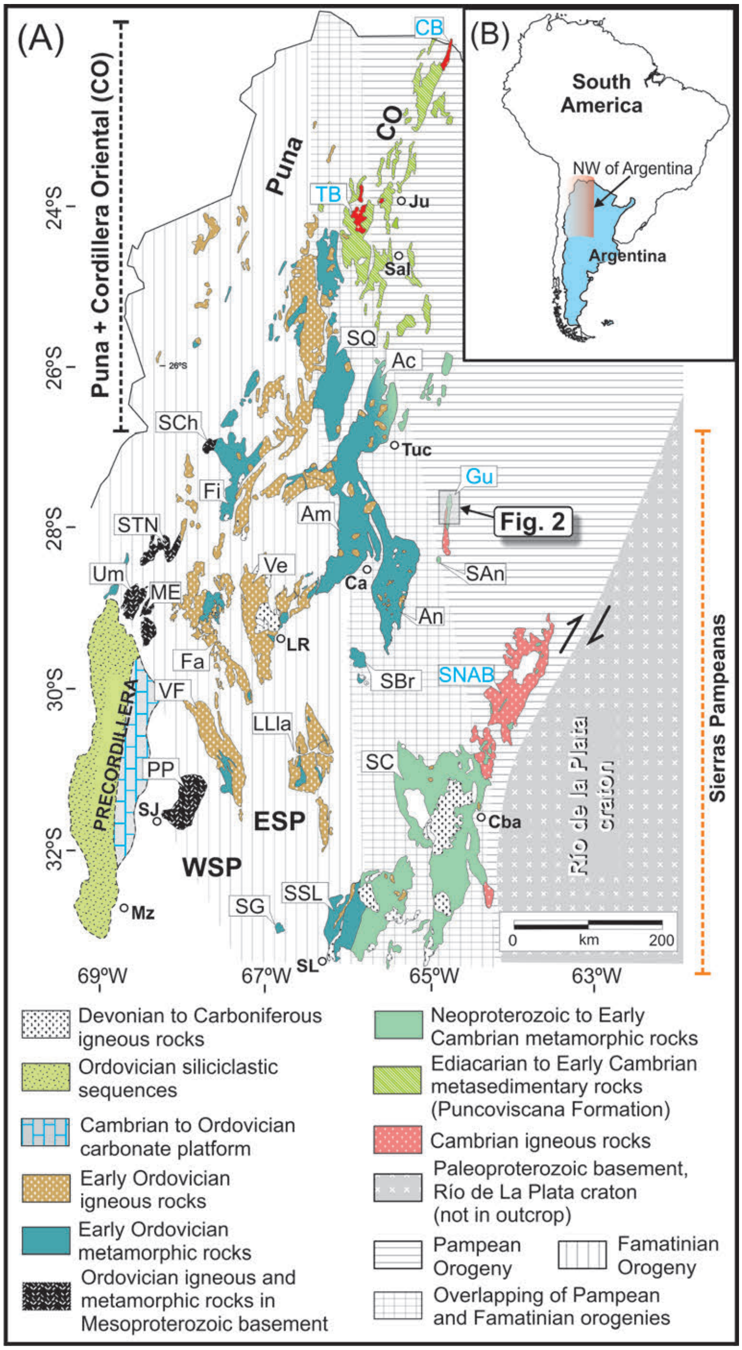

FIG. 1. Schematic geological map of the NW of Argentina including. **A.** Sierras Pampeanas, Western Sierras Pampeanas and Eastern Sierras Pampeanas, (**WSP** and **ESP**) and **B.** Northwestern Argentina (Puna and Eastern Cordillera). Abbreviations: San Salvador de Jujuy (**Ju**), Salta (**Sal**), Tucumán (**Tuc**), La Rioja (**LR**), San Juan (**SJ**), Mendoza (**Mz**), San Luis (**SL**), Catamarca (**Ca**) and Córdoba (**Cba**). Main ranges and Early Cambrian batholith: Cañani batholith (**CB**), Tastil batholith (**TB**), Sierra de Quilmes (**SQ**), Sierra de Aconquija (**Ac**), Sierra de Chuquisaca (**SCh**), Sierra de Fiambala (**Fi**), Sierra de Ambato (**Am**), Sierra de Ancasti (**An**), Sierra de Guasayán (**Gu**), Sierra de Ancaján (**SAn**), Sierra del Toro Negro (**STN**), Sierra de Umango (**Um**), Sierras de Maz-Espinal (**ME**), Sierra de Velasco (**Ve**), Sierra de Famatina (**Fa**), Sierras de Los Llanos (**LLla**) Sierra Brava (**SBr**), Sierra Norte-Ambargasta batholith (**SNAB**), Sierra de Valle Fértil (**VF**), Sierra de Pie de Palo (**PP**), Sierra de Córdoba (**SC**) and Sierra de San Luis (**SSL**) and Sierra del Gigante (**SG**). Inset: rectangle defining study area displayed in the figure 2.

1928) is included in the Eastern Sierras Pampeanas, and it is formed by metamorphic and intrusive granitic rocks (Fig. 2). The metamorphic basement has been subject to petrological and geochemical studies (Blasco *et al.*, 1994; von Gosen *et al.*, 2009), but petrological, geochemical, and geochronological data of the granitic rocks are general and scarce. González and Toselli (1974) reported a Cambrian K-Ar age in biotite (541±7 Ma) for a granitic rock collected in the southern Sierra de Guasayán, near Santa Catalina (Santiago del Estero province). To the best of our knowledge, no further ages have been reported from the Guasayán pluton.

Geochemical and geochronological studies in the Sierras Pampeanas and Eastern Cordillera (Fig. 1) during the past 15 years have improved our

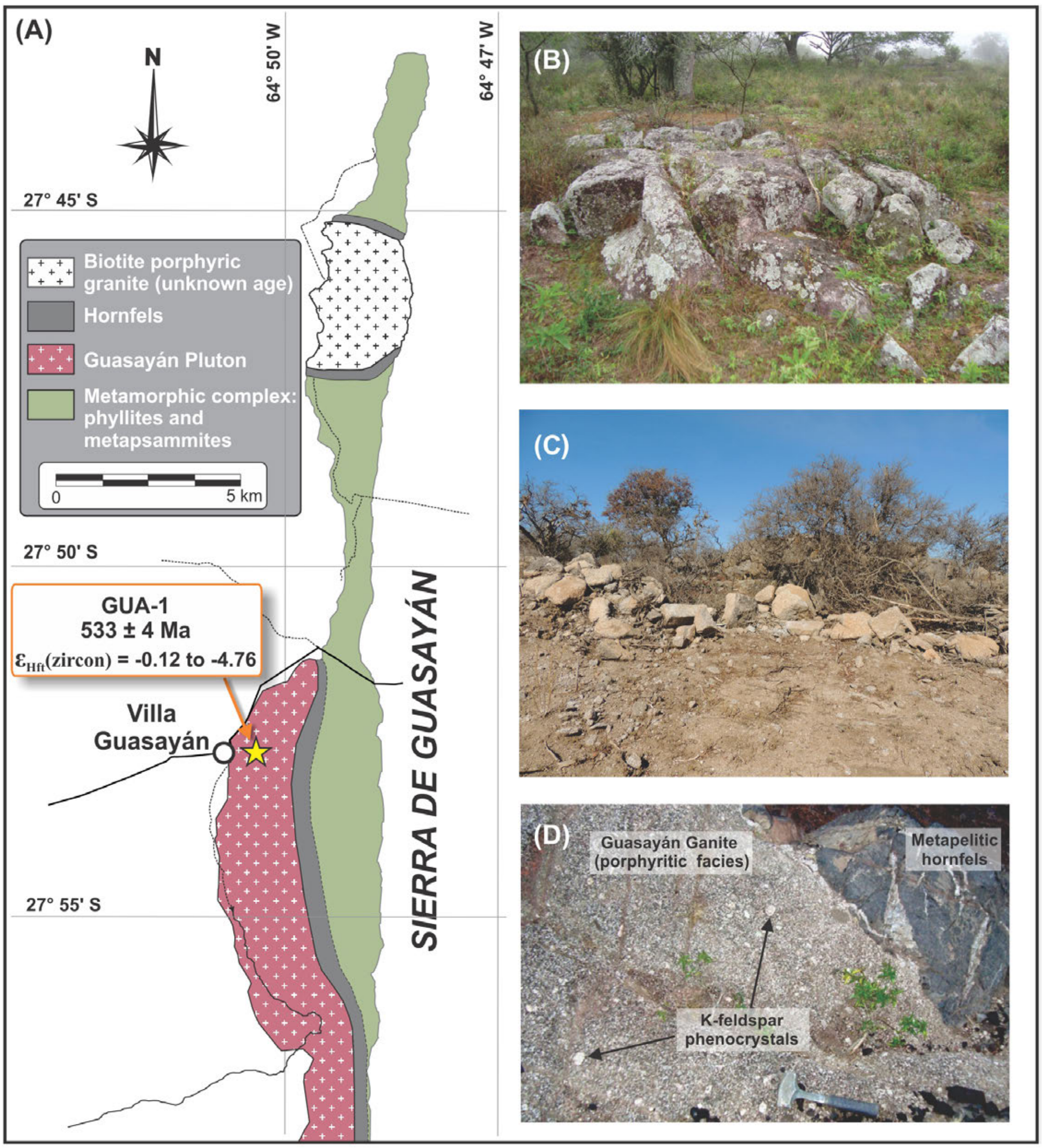

FIG. 2. **A.** Geological map of Guasayán pluton with the location of the dated GUA-1 sample; **B-D.** Outcrops photography of the Guasayán granite.

understanding of the petrogenesis and timing of the Early Cambrian magmatism developed during the Pampean orogeny (*e.g.*, Lira *et al*., 1997; Rapela *et al*., 1998; Omarini *et al*., 2008; Schwartz *et al*., 2008; Hongn *et al*., 2010; Hauser *et al*., 2011; Iannizzotto *et al*., 2013; Lira *et al*., 2014; von Gosen *et al*., 2014 and references therein). These studies were based on the large Sierra Norte-Ambargasta batholith (Fig. 1) and the existence of other outcrops in the Sierras Pampeanas being unproven.

In this paper, we present the first precisely defined age by U-Pb LA-MC-ICP-MS zircon dating, together with complete petrological characterization, and major and trace element data for the dated sample collected from the Guasayán granitic pluton. We also report the first *in situ* Hf isotope data for zircons that crystallized in Early Cambrian granites of the Sierras Pampeanas, in order to evaluate their source.

The geochronological, isotopical, petrological, and geochemical data of the GUA-1 sample from the Guasayán pluton is important in that: **i)** this is the first report of robustly dated Early Cambrian magmatism in Sierra de Guasayán, **ii)** it is the north westernmost example of Early Cambrian magmatism in Sierras Pampeanas and thus might represents the link between the Pampean magmatism of Sierras Pampeanas and Eastern Cordillera in the northwest of Argentina.

2. Petrological and whole-rock chemical characteristics of the Guasayán pluton

The Guasayán pluton is located in the central area of Sierra de Guasayán (Figs. 1 and 2). It was emplaced discordantly in a metamorphic complex. It is mainly composed of interbedded phyllites, metapsammites and scarce calc-silicates layers, displaying a mean NNE-SSW S_1 metamorphic foliation subparallel to primary foliation (S_0). Localized hornfels is developed in the contact with Guasayán Pluton. The hornfels has fine-grained granoblastic texture with biotite+plagioclase+K-feldspar+quartz and probable andalusite (pseudomorphs of muscovite), and zircon, apatite and opaque minerals as accessory minerals. This subsolidus mineral assemblage with andalusite is typical of low-pressure conditions, suggesting a relatively superficial emplacement of the Guasayán pluton.

A porphyritic granitic rock is the dominant facies in the Guasayán pluton, and it crops out in the studied area. It is located in the western area of the pluton (Fig. 2) as a porphyritic biotitic granodiorite, with 3.0×1.5 cm to 2.0×1.0 cm K-feldspar megacrysts in an equigranular matrix formed of quartz, plagioclase and biotite. K-feldspar crystals are oriented and define a dominant N-S magmatic foliation. Biotitic clusters and centimetric basement fragments are recognized in the granite. Similar porphyritic biotitic granites have been recognized in our field works in the southern Sierra de Guasayán (La Punta village).

Petrographic studies of sample GUA-1 reveal that the modal magmatic assemblage is plagioclase (33.0%), quartz (34.3%), K-feldspar (12.3%), biotite (17.5%) with apatite and zircon as accessory minerals (~1.85%). The modal data in the Streckeisen (1976) diagram indicate that the granitic rock is a granodiorite. Chlorite is a common secondary mineral associated with biotite. Scarce secondary epidote occurs associated with biotite and chlorite. Two main varieties of plagioclase were recognized: **a)** coarse-grained (Pl_a, 8.0×5.0 mm; minerals abbreviation after Whitney and Evans 2010 and size of individual grains from Hibbard 1995), tabular and mostly subhedral crystals, showing optical zoning and polysynthetic twinning; **b)** medium-grained: Pl_b, ranging from 5.0×2.0 mm to 4.0×2.0 mm; and Pl_c, ranging from 2.0×2.0 mm to 2.4×1.2, forming tabular and mostly subhedral crystals with polysynthetic twins. Pl_a is scarce whereas Pl_b and Pl_c occurs evenly distributed throughout the rock. Systematic analysis using electron microprobe reveals compositions ranges from $An_{47.0}$ to $An_{33.2}$, $An_{33.2}$ to $An_{23.6}$, and $An_{21.5}$ to $An_{20.3}$, for Pl_a, Pl_b, and Pl_c, respectively. The alkali feldspar is perthite, medium-grained, ranging from 3.0×1.5 mm to 4×2 mm, and forms tabular or irregular subhedral-anhedral crystals, with distinctive perthitic texture. Feldspar is interstitial to the crystalline framework. The composition of alkali feldspar is uncertain since the abundance of perthite prevents determination of the original Na_2O content, leading to a low total.

The quartz has mostly irregular form and two sizes are recognized: (a) coarse-grained (Qtz_a 4.2×2.0 mm) and medium-grained (Qtz_b, 2.2×1.0 mm).

Biotite has variable size, ranging from 3.0×1.0 mm to 1.3×1.0 mm, and is frequently found forming clusters. It occurs as subhedral plates or irregular sections with light-to-dark brown pleochroism and abundant inclusions of apatite and zircon. In terms of Al^{IV} *versus* ($XFe=[Fe^{2+}/(Fe^{2+}+Mg)]$) the biotites show relatively high siderophyllite-eastonite content (average Al^{IV}=2.53 atom/formula unit and XFe=0.65) together with moderate to low F contents (average F=0.38 wt%, n=5).

Fluorapatite is an abundant accessory mineral; it is euhedral to subhedral with dominant hexagonal and short prismatic forms. It is variably fine-grained, 0.3 to 1.0 mm of diameter or 1.1×0.3 mm (short prismatic), and is commonly observed as inclusions in biotite.

Systematic analysis using the electron microprobe (determining Zr and LREE data) reveals the presence of two radioactive minerals, zircon and monazite, as well as the occurrence of small-scale ilmenite and magnetite crystals (no greater than 100 μm), all mostly included in biotite.

The data show that the dated granitic rock can be classified in the TAS and diagram (figure not included, data in Table 1) as subalkaline felsic granodiorite, with 69% SiO_2. For similar SiO_2 content this rock has comparable composition to those commonly observed in calc-alkaline rocks of the Pampean magmatism in the Sierras Pampeanas (*e.g.*, Iannizzotto *et al.*, 2013) with CaO=2.45%, total alkalis (7.08%), CaO/K_2O=0.59, Na_2O/ K_2O=0.71, and [FeO^t/(FeO^t+MgO)]=0.78 (*i.e.*, magnesian granite) (Table 1). The porphyritic monzogranite has an alumina saturation index (ASI) of 1.05 (see Table 1) similar to other metaluminous calc-alkaline monzogranites, with a relatively low agpaitic index of 0.65.

In the spider-diagram (figure not included, data in Table 1) the sample GUA-1 shows depletion in Nb, Ti and Sr and enrichment in Ba, Rb, Th and K, typically characteristic of Pampean calc-alkaline magmatism (Iannizzotto *et al.*, 2013). The total rare earth element (REE) total abundance is 204 ppm (Table 1), with moderate slope (La_N/Yb_N=8.05) and slightly negative Eu anomaly (Eu/Eu*=0.76).

3. U-Pb geochronology and Hf isotopes data

A representative sample (GUA-1) from Sierra de Guasayán was analysed for whole-rock major and trace elements using a ThermoARL sequential X-ray fluorescence spectrometer, following the procedure described by Johnson *et al.* (1999). Trace element compositions were determined using an Agilent 7700 ICP-MS, following the procedure described in http://cahnrs.wsu.edu/soe/facilities/geolab/technotes/icp-ms_method/ (last visit 20-11-2015). The data is included in Table 1.

TABLE 1. MAJOR AND TRACE ELEMENT WHOLE-ROCK DATA FOR THE SAMPLE GUA-1.

Igneous unit Sample	Gusayán pluton GUA-1
wt%	
SiO_2	69.24
TiO_2	0.65
Al_2O_3	14.44
FeO^t	4.01
MnO	0.07
MgO	1.12
CaO	2.45
Na_2O	2.95
K_2O	4.13
P_2O_5	0.20
LOI (%)	0.42
TOTAL	99.69
ppm	
Cs	10.3
Rb	151
Sr	143
Ba	613
La	40.6
Ce	80.3
Pr	9.87
Nd	38.5
Sm	8.32
Eu	1.97
Gd	7.55
Tb	1.18
Dy	6.81
Ho	1.35
Er	3.61
Tm	0.532
Yb	3.37
Lu	0.512
U	1.89
Th	12.09
Y	35.33
Nb	16.35
Zr	245
Hf	6.62
Ta	1.34
Ga	20
XFe	0.78
$(La/Yb)_N$	8.05
Eu/Eu*	0.76
ASI	1.05
AI	0.65

Analytical details are found in the text. Total iron as FeO. XFe=[FeO^t/(FeO^t+MgO)]. **ASI:** Aluminum Saturation Indices=Al_2O_3/[(CaO+Na_2O+K_2O] (mol).

LA-MC-ICP-MS U-Pb analysis of separated zircons from GUA-1 (Table 2) sample was carried out at the Geochronological Research Center, Sao Paulo University, Brazil, using a 193 nm excimer laser (Photon Machines) coupled to a Neptune multicollector, double-focusing, magnetic sector ICP-MS. Operating procedures and parameters are discussed by Sato *et al*. (2011). Fractionation in the plasma was corrected by normalizing U-Pb and Pb-Pb ratios of the unknowns to those of zircon standards (GJ 1, $^{206}Pb/^{238}Pb$ age by IDTIMS = 599.8±2.4 Ma).

In-situ LA-MC-ICP-MS Lu-Hf isotope analyses were conducted at Geochronological Research Center, Sao Paulo University, Brazil using Photon laser system (Sato *et al*., 2010) coupled to a Thermo-Finnigan Neptune MC-ICP-MS with 9 Faraday collectors. Lu-Hf isotopic analyses reported here were performed on the same zircon domains that were previously dated (Table 3). Laser operating conditions are reported in Table 3.

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TABLE 2. U-Pb LA-MC-ICP-MS ZIRCON RESULTS FOR GUA-1, GUASAYÁN PLUTON.

		Ratios				Ages			
Grain/ Spot	**GCh SS**	**$^{238}U/^{206}Pb$**	**1σ**	**$^{207}Pb/^{206}Pb$**	**1σ**	**$^{206}Pb/^{238}U$**	**1σ**	**$^{207}Pb/^{206}Pb$**	**1σ**
2.1	e, p, osc	11.7691	0.1628	0.0564	0.0020	526	0.007	470	0.077
5.1	e, p, osc	11.6819	0.1880	0.0561	0.0029	529	0.008	456	0.106
7.1	e, p, osc	11.7740	0.1627	0.0574	0.0021	525	0.007	505	0.083
8.1	e, p/fr, osc	11.4686	0.1660	0.0566	0.0021	539	0.007	476	0.081
10.1	e, p, osc	11.3888	0.1490	0.0577	0.0018	543	0.007	520	0.068
11.1	e, p, osc	11.5700	0.1801	0.0587	0.0027	534	0.008	554	0.104
15.1	e, p, osc	11.7634	0.1532	0.0573	0.0018	526	0.007	502	0.069
16.1	e, p, osc	11.4484	0.1682	0.0570	0.0025	540	0.008	493	0.094
17.1	e, p, osc	11.7352	0.1616	0.0577	0.0021	527	0.007	519	0.080
18.1	e, p, osc	11.5385	0.1775	0.0576	0.0026	536	0.008	516	0.103
19.1	e, p, osc	11.5373	0.1713	0.0567	0.0024	536	0.008	480	0.094
23.1	e, p, osc	11.5327	0.1508	0.0582	0.0020	536	0.007	538	0.077
13.1 (inh-age)	e, p, c	6.1830	0.0807	0.0696	0.0020	966	0.012	916	0.058
14.1 (inh-age)	e, p, m	9.9660	0.1214	0.0579	0.0017	616	0.007	527	0.064

$^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios corrected for static fractionation using GJ 1.
Measurement errors represent within-run uncertainty only. All data points were used in calculated concordia age.
Grain characteristics (GCh) and site of the spot (SS): Site of the spot: **e:** end or edge. Habit of the grain: **p:** prism, **fr:** fragmented.
Cathodoluminescence images: **osc:** oscillatory zoning. **inh-age:** inheritance age.
Location of sample is: 27°53’ 08.1’’ and 64°50’ 35.2’’.

TABLE 3. LASER ABLATION HF ISOTOPE DATA FOR IGNEOUS DATED ZIRCONS FROM GUA-1, GUASAYÁN PLUTON.

Grain/spot	$^{176}Hf/^{177}Hf$	± 2 σ	$^{176}Lu/^{177}Hf$	± 2 σ	εHf (t)	T_{DM} (Ga)
2.1	0.282319	0.000045	0.001339	0.000016	-4.76	1.74
5.1	0.282358	0.000047	0.001270	0.000019	-3.32	1.65
7.1	0.282393	0.000035	0.001011	0.000002	-1.98	1.56
10.1	0.282387	0.000032	0.000779	0.000010	-2.13	1.57
15.1	0.282425	0.000032	0.000971	0.000026	-0.84	1.49
16.1	0.282420	0.000032	0.000820	0.000060	-0.97	1.50
17.1	0.282447	0.000044	0.001190	0.000010	-0.12	1.45
23.1	0.282399	0.000039	0.001302	0.000001	-1.89	1.56

Laser operating conditions: GJ1-6mJou 8.55J/cm2 (100%), 7Hz, spot=39µm, He (MCF1)=0.25l/min, (MCF2)=0.5L/min, N2=1.2mL/min, 50 ciclos, AR80=30V.
t: crystallization age (533 Ma), **T:** model age.
Present-day and initial εHft values were calculated using CHUR compositions of $^{176}Hf/^{177}Hf$today=0.282772 and $^{176}Lu/^{177}Hf$=0.0332 (Blichert-Toft and Albarede, 1997) and a ^{176}Lu decay constant of $1.867e^{-11}$ (Söderlund *et al.*, 2004; Scherer *et al.*, 2007). Average crustal $^{176}Lu/^{177}Hf$ of 0.015 (Goodge and Vervoort, 2006). Depleted mantle (DM) parameters from (Vervoort and Blichert-Toft, 1999). $^{176}Hf/^{177}Hf_{CHUR(t)}$=0.282439.

The combined SEM-CL and optical images reveal that the zircons separated from GUA-1 are mostly elongate prismatic grains with oscillatory zoning and subhedral to euhedral-terminations. Analysis spots were mostly located in the outer oscillatory zoning and the majority of the zircon ages are concentrated at about 533 Ma (see Table 2). Twelve data points yield a Tera-Wasserburg Concordia age (Ludwig, 2003) of 533±4 Ma (2σ confidence limits, allowing for the uncertainty in U-Pb calibration). This is considered the best estimate for the crystallization of the host felsic granodiorite (Fig. 3). Two inheritance ages ("Grenvillian" and "Brazilian") were obtained from zircon core (966 Ma and 616 Ma, Table 2 and Fig. 3).

The Early Cambrian zircons have variable ε_{Hft} (t=533 Ma) values ranging from -0.12 to -4.76. The average model age is calculated as 1.56 Ga (Table 3 and Fig. 4).

4. Discussion

Petrological and whole-rock geochemical indicate that GUA-1 is a subalkaline porphyritic biotite monzogranite. Frost *et al*. (2001) and Frost and Frost (2011) have provided exhaustive analysis and classification of granitic suites based on a range of major element indices. According to the Frost *et al*. (2001) classification scheme, GUA-1 is dominantly magnesian-type and it is projected close to the boundary separating calcic and calc-alkalic series in the modified alkaline-lime index of Peacock (1931) (figures not included, data in Table 1). This composition is those reported in classical calc-alkaline magmatism (Frost *et al*., 2001, Frost and Frost, 2011). As mentioned in the Section 2, sample GUA-1 shows depletion in Nb, Ti, Ta and Sr and enrichment in Ba, Rb, Th and K typical of magmas formed in Pampean subduction zone.

González and Toselli (1974) reported a Cambrian K-Ar age in biotite (541±7 Ma) for a granitic rock collected in the eastern flank of the Sierra de Guasayán, near Santa Catalina (Santiago del Estero province), located 25 km to the southeast of the studied area. To the best of our knowledge, no further ages have been reported from the Guasayán pluton.

Recent petrological and geochronological (U-Pb SHRIMP zircon ages) studies in the Sierra Norte-Ambargasta batholith (Iannizzotto *et al*., 2013) indicate an episodic intrusion history: **i)** an early stage constrained to 537-530 Ma, and **ii)** a second stage with post-kinematic peraluminous magmatism emplazed between 530-520 Ma. The earlier, dominant group was derived largely from metaluminous calc-alkaline subduction-related magmas, whereas

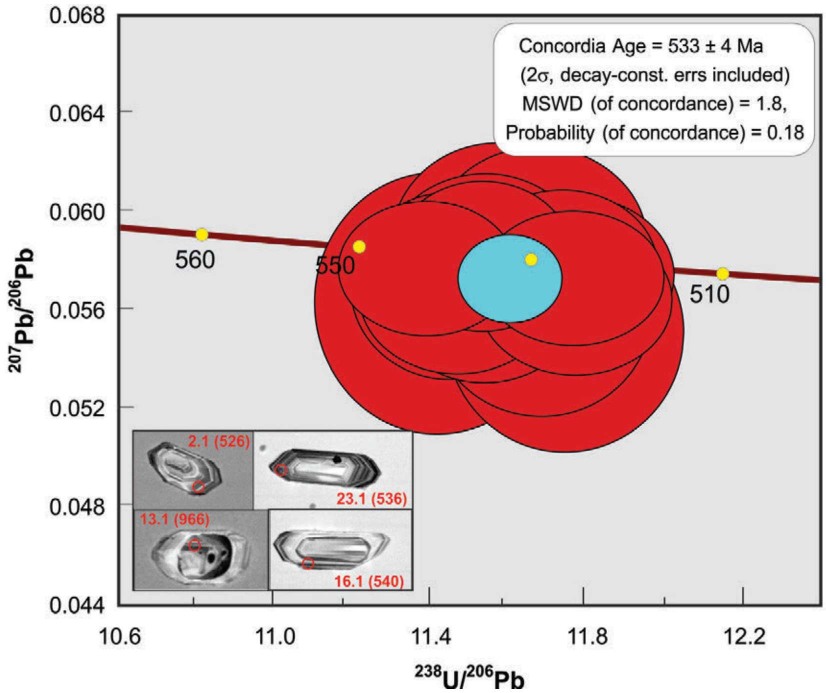

FIG. 3. U-Pb LA-MC-ICP-MS zircon dating of GUA-1 sample from Guasayán pluton. The main Tera-Wasserburg plot shows most analyses plotting between 526 and 540 Ma and the inset shows a Concordia age of 533±4 Ma. Selected zircon images are also shown. Data reported in Table 2.

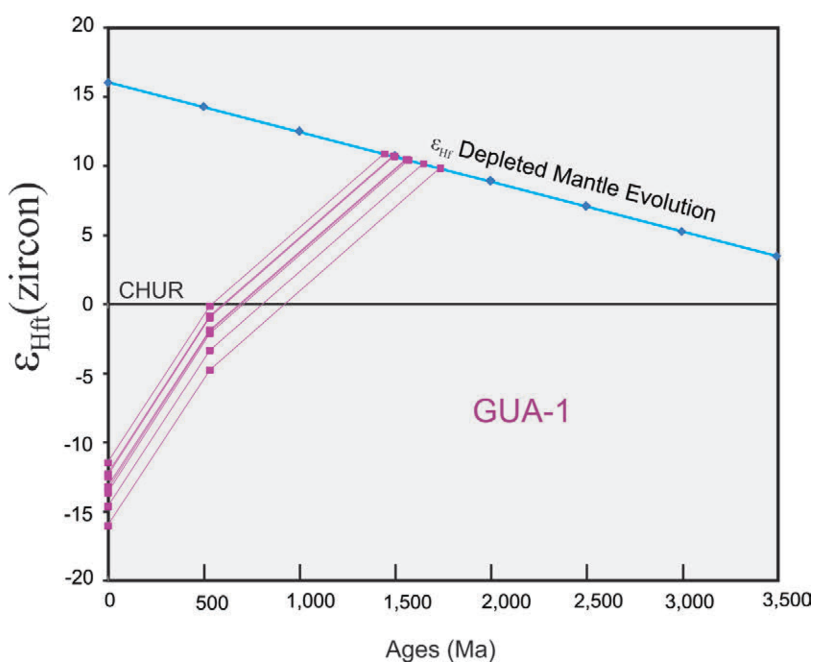

FIG. 4. Age *versus* ε_{Hft} values for Early Cambrian zircon hosted in GUA-1 granite, showing both measured and initial epsilon Hf values as function of crystallization age. Depleted-mantle Hf evolution curve from Vervoort and Blichert-Toft (1999).

the late granites are peraluminous and they have been linked with a post-collisional event. The geochronological data (533±4 Ma) from the Guasayán pluton indicate that this pluton could be included in early stage of the Pampean magmatism.

In the Eastern Cordillera, northwest of Argentina, the metaluminous to slightly peraluminous, Tastil batholith yield two U-Pb LA-MC-ICP-MS zircon ages of 534±7 Ma and 541±4 Ma, for the grey and red granitic facies, respectively (Hauser *et al*., 2011), and can be also assigned to the early Pampean magmatism. Thus, the crystallization age obtained from the Guasayán pluton is similar to those reported for Pampean granites of Sierra Norte-Ambargasta and Tastil batholith.

The Guasayán pluton might provide a link between Early Cambrian magmatism of the central Sierras Pampeanas and that of the Eastern Cordillera, contributing to define the western boundary of the Pampean paleo-arc (Fig. 5).

Additionally, the studied area is relevant because the Famatinian and Pampean magmatic belts are close to each other in this area. In the Sierra de Ancasti (located to the west of the Sierra de Guasayán;

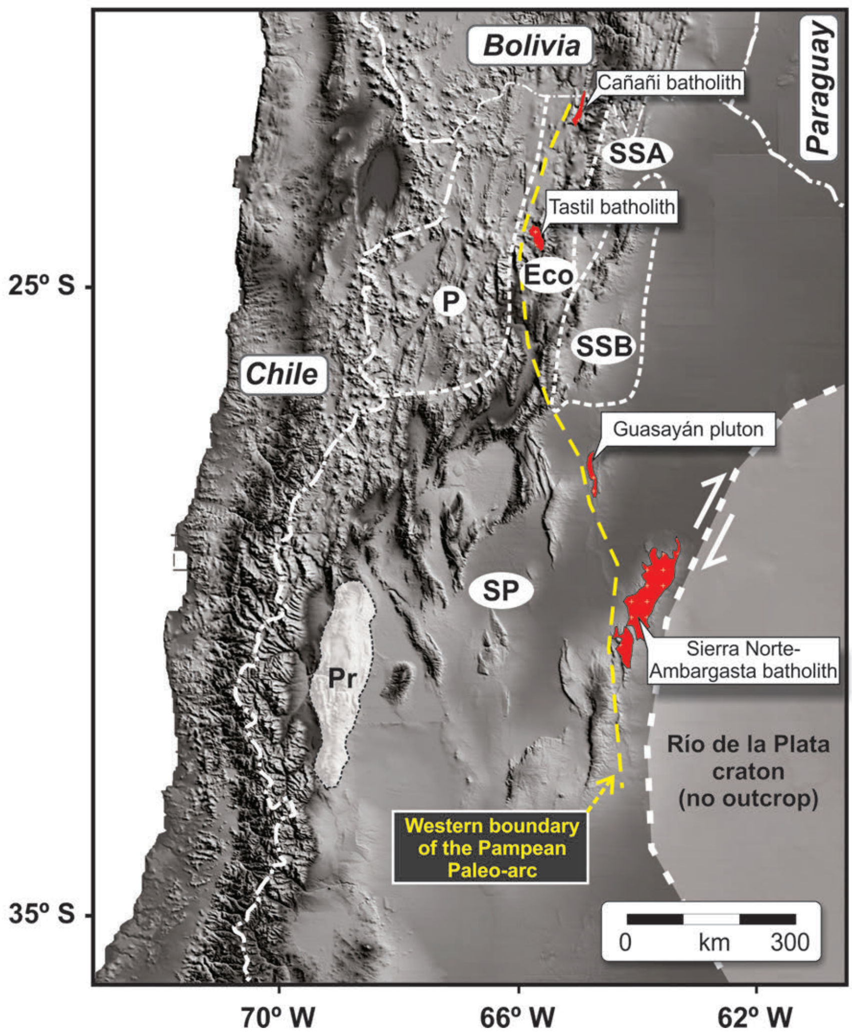

FIG. 5. Inferred western boundary of the Pampean paleo-arc. Abbreviations for the geological provinces of Argentina: **Pr:** Precordillera, **SP:** Sierras Pampeanas, **SSB:** Sistema de Santa Bárbara, **SSA:** Sierras Subandinas, **Eco:** Eastern Cordillera, **P:** Puna. Cañani batholith=523±5 Ma (Escayola *et al*., 2011).

Fig. 1), a precise Famatinian U-Pb age in zircon using LA-ICP-MS was reported by Dahlquist *et al*. (2012) but Pampean magmatism is absent. Conversely, Famatinian magmatism is not recognized in the Sierra de Guasayán where Pampean magmatism is now known (Fig. 1).

The ε_{Hft} values for magmatic zircons are reported in Table 3 and Fig. 4. As in the general study reported by Kemp *et al*. (2007), an important feature of the Hf isotope data is the significant range of ε_{Hft} values exhibited by zircons within the same sample (up to 10 ε units). Such scatter can be in part because zircon can crystallize very early and retain vestiges of the original (*e.g.*, juvenile) Hf isotope signature (Kemp *et al*., 2007; Dahlquist *et al*., 2013), whereas the $^{176}Hf/^{177}Hf$ ratio of the melt from which the zircons precipitated might change from early to late crystallization stages due to progressive assimilation of crustal material. The ε_{Hft} values reported here suggest interaction between juvenile and continental material, although the latter appear to be dominant. Thus, a petrogenetic model invoking interaction between a juvenile magma and crustal material of probable Early Mesoproterozoic age (see T_{DM} in Table 3) could explain evolution of the parental magma of the Guasayán pluton. Alternatively, a heterogeneous crust could be assumed as the source of the parental magma (Villaros *et al*., 2012).

Hf isotope data were reported by Hauser *et al*. (2011) for Early Cambrian granites of the Tastil batholith with ε_{Hft} (t=534 Ma) ranging from +1.1 to -6.9 (n=7) although most are in the range -1.5 to -1.8, with an average T_{DM}=1.45 Ga. Thus, the Hf isotope zircons data suggest that the Guasayán and Tastil granites have significant crustal participation in the source.

Hf isotope zircons data are unavailable for the granites of Sierra Norte-Ambargasta batholith. Initial $^{87}Sr/^{86}Sr$ ratios and ε_{Ndt} values (Iannizzotto *et al*., 2013) are notably variable ranging from 0.706 to 0.710 and -1.8 to -5.9, respectively. In some cases inherited 600 Ma and 970 Ma zircon were founded, similar to the isotopic and zircon provenance seen in the metamorphic host rocks (Iannizzotto *et al*., 2013). The variable initial $^{87}Sr/^{86}Sr$ ratios and ε_{Ndt} values could be explained assuming a hypothetical interaction between dominant crustal and juvenile material or heterogeneous crust, although Hf isotope data are required to establish a robust petrogenetic model.

5. Conclusions

1. The whole-rock chemical data from GUA-1 suggest that this pluton is a metaluminous subalkaline felsic granodiorite. The first precise U-Pb LA-MC-ICP-MS zircon age from GUA-1 indicate that the Guasayán pluton was emplaced in Early Cambrian time, 533±4 Ma. The Guasayán pluton is the north westernmost outcrop of the Early Cambrian magmatism in the Sierras Pampeanas.
2. Based on Hf in zircon isotope data, an interaction between dominant crust of hypothetical Early Mesoproterozoic ages and juvenile magmas could be applied to the generation of the parental magma of the Guasayán pluton. Alternatively, a heterogeneous crust could be assumed as the source of the parental magma. Hf in zircon isotope data reported for the granites of the Tastil batholith suggest a similar petrogenetic process involving significant crustal participation.
3. The new age from Guasayán pluton might contribute to define the western boundary of the Pampean paleo-arc between the Sierras Pampeanas and the Eastern Cordillera.

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References

Basei, M.A.S.; da Costa Campos Neto, M.; Pacheco Lopes, A.; Nutman, A.P.; Liu, D.; Sato, K. 2013. Polycyclic evolution of Camboriú Complex migmatites, Santa Catarina, Southern Brazil: integrated Hf isotopic and U-Pb age zircon evidence of episodic reworking of a Mesoarchean juvenile crust. Brazilian Journal of Geology 43: 427-443.

Beder, R. 1928. La Sierra de Guasayán y sus alrededores. Publicación de la Dirección General de Minas, Geología e Hidrogeología 39: 171 p.

Blasco, G.; Caminos, R.L.; Lapido, O.; Lizuaín, A.; Martínez, H.; Nullo, F.; Panza, J.L.; Sacomani, L. 1994. Hoja Geológica 2966-II, San Fernando del Valle de Catamarca, provincias de Catamarca, Santiago del Estero y Tucumán. Programa nacional de cartas geológicas de la República Argentina, 1:250.000, SEGEMAR: 50 p.

Blichert-Toft, J.; Albarede, F. 1997. The Lu-Hf isotope geochemistry of chondrites and the evolution of the mantle-crust system. Earth and Planetary Science Letters 148: 243-258.

Caminos, R. 1972. Sierras Pampeanas de Catamarca, Tucumán, La Rioja y San Juan. *In* Simposio de Geología Regional Argentina, No. 2 (Leanza, A.F.; editor). Academia Nacional de Ciencias de Córdoba 1: 41-79. Córdoba.

Casquet, C.; Baldo, E.G.; Pankhurst, R.J.; Rapela, C.W.; Galindo, C.; Fanning, C.M.; Saavedra, J. 2001. Involvement of the Argentine Precordillera terrane in the Famatinian mobile belt: U-Pb SHRIMP and metamorphic evidence from the Sierra de Pie de Palo. Geology 29: 703-706.

Dahlquist, J.A.; Rapela, C.W.; Pankhurst, R.J.; Fanning, C.M.; Vervoort, J.D.; Hart, G.; Baldo, E.G.; Murra, J.A.; Alasino, P.H.; Colombo, F. 2012. Age and magmatic evolution of the Famatinian granitic rocks of Sierra de Ancasti, Sierras Pampeanas, NWArgentina. Journal of South American Earth Sciences 34: 10-25.

Dahlquist, J.A.; Pankhurst, R.J.; Gaschnig, R.M.; Rapela, C.W.; Casquet, C.; Alasino, P.H.; Galindo, C.; Baldo, E.G. 2013. Hf and Nd isotopes in Early Ordovician to Early Carboniferous granites as monitors of crustal growth in the Proto-Andean margin of Gondwana. Gondwana Research 23: 1617-1630.

Dahlquist, J.A.; Alasino, P.H.; Bello, C. 2014. Devonian F-rich peraluminous A-type magmatism in the proto-Andean foreland (Sierras Pampeanas, Argentina): geochemical constraints and petrogenesis from the western-central region of the Achala batholiths. Mineralogy and Petrology 108: 391-417.

Escayola, M.P.; Pimentel, M.; Armstrong, R. 2007. Neoproterozoic backarc basin: sensitive high-resolution ion microprobe U-Pb and Sm-Nd isotopic evidence from the Eastern Pampean Ranges, Argentina. Geology 35: 495-498.

Escayola, M.P.; van Staal, C.R.; Davis, W.J. 2011. The age and tectonic setting of the Puncoviscana Formation in northwestern Argentina: an accretionary complex related to Early Cambrian closure of the Puncoviscana Ocean and accretion of the Arequipa-Antofalla block. Journal of South American Earth Sciences 32: 438-459.

Frost, B.R.; Barnes, C.G.; Collins, W.J.; Arculus, R.J.; Ellis, S.J.; Frost, C.D. 2001. A geochemical classification for granitic rocks. Journal of Petrology 42: 2033-2048.

Frost, C.D.; Frost, B.R. 2011. On Ferroan (A-type) Granitoids: their compositional variability and modes of origin. Journal of Petrology 52: 39-53.

González, R.R.; Toselli, A.J. 1974. Radimetric dating of igneous rocks from Sierras Pampeanas, Argentina. Geociencias 4 (3): 137-141. San Pablo, Brasil.

Goodge, J.W.; Vervoort, J.D. 2006. Origin of Mesoproterozoic A-type granites in Laurentia: Hf isotope evidence. Earth and Planetary Science Letters 243: 711-731.

Hauser, N.; Matteini, M.; Omarini, R.; Pimentel, M. 2011. Combined U-Pb and Lu-Hf isotope data on turbidites of the Paleozoic basement of NW Argentina and petrology of associated igneous rocks: Implications for the tectonic evolution of western Gondwana between 560 and 460 Ma. Gondwana Research 19: 100-127.

Hibbard, M.J. 1995. Petrography to petrogenesis. Prentice Hall: 587 p. USA.

Hongn, F.D.; Tubia, J.M.; Aranguren, A.; Vegas, N.; Mon, R.; Dunning, G. 2010. Magmatism coeval with lower Paleozoic shelf basins in NW-Argentina (Tastil batholith): constraints on current stratigraphic and tectonic interpretations. Journal of South American Earth Sciences 29: 289-305.

Iannizzotto, N.F.; Rapela, C.W.; Baldo, E.G.A.; Galindo, C.; Fanning, C.M.; Pankhurst, R.J. 2013. The Sierra Norte-Ambargasta batholith: Late Ediacaran-Early Cambrian magmatism associated with Pampean transpressional tectonics. Journal of South American Earth Sciences 42: 127-143.

Johnson, D.M.; Hooper, P.R.; Conrey, R.M. 1999. XRF analysis of rocks and minerals for major and trace elements on a single low dilution Litetraborate fused bead. Advances in X-ray Analysis 41: 843-867.

Kemp, A.I.S.; Hawkesworth, C.J.; Foster, G.L.; Paterson, G.A.; Woodhead, J.D.; Hergt, J.M.; Gray, C.M.; Whitehouse, M.J. 2007. Magmatic and crustal differentiation history of granitic rocks from Hf-O isotopes in zircon. Science 315: 980-983.

Lira, R.; Millone, H.A.; Kirschbaum, A.M.; Moreno, R.S. 1997. Calc-alkaline arc granitoid activity in the Sierra Norte-Ambargasta Ranges, Central Argentina. Journal of South American Earth Sciences 10: 157-177.

Lira, R.; Poklepovic, M.F.; O'Leary, M.S. 2014. El magmatismo cámbrico en el batolito de Sierra Norte-Ambargasta. *In* Geología y Recursos Naturales de la Provincia de Córdoba (Martino, R.; Guereschi, A.; editors). Asociación Geológica Argentina: 183-216. Córdoba.

Ludwig, K.R. 2003. Isoplot/Ex Version 3.0: a Geochronological Toolkit for Microsoft Excel. Berkeley Geochronology Center, Special Publication No. 4. USA.

Omarini, R.H.; Sureda, R.; Toselli, A.J.; Rossi, J.N. 1999. Ciclo Pampeano-Proterozoico superior-Eocámbrico: Magmatismo. *In* Relatorio del Congreso Geológico Argentino, No. 14 (González Bonorino, G.; Omarini, R.; Viramonate, J.; editores). Actas tomo I: 29-40. Salta.

Omarini, R.H.; Sureda, R.J.; López de Azarevich, V.L.; Hauser, N. 2008. El basamento Neoproterozoico-Cámbrico inferior en la provincia de Jujuy. *In* Relatorio del Congreso Geológico Argentino. Geología y Recursos Naturales de la provincia de Jujuy, No. 17 (Coira, B.; Zappettini, E.; editors). Ciclo Pampeano y Famatiniano: 17-28. San Salvador de Jujuy.

Peacock, M.A. 1931. Classification of igneous rock series. Journal of Geology 39: 54-67.

Rapela, C.W.; Pankhurst, R.J.; Casquet, C.; Baldo, E.; Saavedra, J.; Galindo, C.; Fanning, C.M. 1998. The Pampean Orogeny of the Southern proto-Andes: Cambrian continental collision in the Sierras de Córdoba. *In* The Proto-Andean Margin of Gondwana (Pankhurst, R.J.; Rapela, C.W.; editors). Geological Society of London, Special Publication 142: 181-217.

Rapela, C.W.; Pankhurst, R.J.; Casquet, C.; Fanning, C.M.; Baldo, E.G.; González-Casado, J.M.; Galindo, C.; Dahquist, J. 2007. The Río de la Plata craton and the assembly of SW Gondwana. Earth Sciences Review 83:49-82.

Rapela, C.W.; Pankhurst, R.J.; Casquet, C.; Baldo, E.; Galindo, C.; Fanning, C.M.; Dahlquist, J.A. 2010. The Western Sierras Pampeanas: protracted Grenville-age history (1330-1030 Ma) of intra-oceanic arcs, subduction-accretion at continental-edge and AMCG intraplate magmastism. Journal of South American Earth Sciences 29: 105-127.

Rapela, C.W.; Verdecchia, S.O.; Casquet, C.; Pankhurst, R.J.; Baldo, E.G.; Galindo, C.; Murra, J.A.; Dahlquist, J.A.; Fanning, C.M. 2015. Identifying Laurentian and SW Gondwana sources in the Neoproterozoic to Early Paleozoic metasedimentary rocks of the Sierras Pampeanas: paleogeographic and tectonic implications. Gondwana Research. doi:10.1016/j.gr.2015.02.010.

Sato, A.M.; González, P.D.; Llambías, E.J. 2003. Evolución del Orógeno Famatiniano en la Sierra de San Luis: magmatismo de arco, deformación y metamorfismo de bajo a alto grado. Revista de la Asociación Geológica Argentina 58: 487-504.

Sato, K.; Siga, Jr.; O.; Silva, J.A.; McReath, I.; Liu, D.; Iizuka, T.; Rino, S.; Hirata, T.; Sproesser, W.M.; Basei, M.A.S. 2009. In situ isotopic analyses of U and Pb in zircon by remotely operated SHRIMP II, and Hf by LA-ICP-MS: an example of dating and genetic evolution of zircon by $^{176}Hf/^{177}Hf$ from the Ita Quarry in the Atuba Complex, SE Brazil. Geologia Universidade São Paulo, Série Cientifica São Paulo 9: 61-69.

Sato, K.; Basei, M.A.S.; Ferreira, C.M.; Vlach, S.R.F.; Ivanuch, W.; Siga, Jr.; O.; Onoi, A.T. 2010. *In situ* U-Th-Pb isotopic analyses by Excimer laser ablation/ICP-MS on Brazilian xenotime megacrystal: first U-Pb results at CPGeo-IG-USP. *In* South American Symposium on Isotope Geology, No. 7: CD Room. Brasília, DF.

Sato, K.; Basei, M.A.S.; Ferreira, C.M.; Sproesser, W.M.; Vlach, S.R.F.; Ivanuch, W.; Onoi, A.T. 2011. U-Th-Pb analyses by excimer laser ablation/ICP-MS on MG Brazilian xenotime. Goldschmidt-2011. Mineralogical Magazine: 1801 p.

Scherer, E.; Whitehouse, M.J.; Münker, C. 2007. Zircon as a monitor of crustal growth. Elements 3: 19-24.

Schwartz, J.J.; Gromet, L.P. 2004. Provenance of Late Proterozoic-early Cambrian basin, Sierras de Córdoba, Argentina. Precambrian Research 129: 1-21.

Schwartz, J.; Gromet, L.; Miro, R. 2008. Timing and duration of the calc-alkaline arc of the Pampean orogeny implications for the Late Neoproterozoic to Cambrian evolution of Western Gondwana. Journal of Geology 116: 39-61.

Söderlund, U.; Patchett, J.P.; Vervoort, J.D.; Isachsen, C.E. 2004. The ^{176}Lu decay constant determined by Lu-Hf and U-Pb isotope systematics of Precambrian mafic intrusions. Earth and Planetary Science Letters 219: 311-324.

Streckeisen, A. 1976. To each plutonic rock its proper name. Earth-Science Reviews 13: 1-33.

Toselli, A.J. 1990. Metamorfismo del Ciclo Pampeano. *In* El Ciclo Pampeano en el Noroeste Argentino (Aceñolaza, F.G.; Miller, H.; Toselli, A.J.; editors). Universidad Nacional de Tucumán, Serie Correlación Geológica 4: 181-198.

Turner, J.C.M. 1960. Estratigrafía de la Sierra de Santa Victoria y adyacencias. Academia Nacional de Ciencias Córdoba, Boletín 41: 163-196. Córdoba.

Varela, R.; Basei, M.A.S.; González, P.D.; Sato, A.M.; Naipauer, M.; Campos Neto, M.C.A.; Meira, V.T. 2011. Accretion of Grenvillian terranes to the southwestern border of the Río de La Plata craton, western Argentina. International Journal Earth Sciences (Geol Rundsch) 100: 243-272.

Vervoort, J.D.; Blichert-Toft, J. 1999. Evolution of the depleted mantle: Hf isotope evidence from juvenile rocks through time. Geochimica et Cosmochimica Acta 63: 533-556.

Villaros, A.; Buick, I.S.; Stevens, G. 2012. Isotopic variations in S-type granites: an inheritance from a heterogeneous source? Contributions to Mineralogy and Petrology163: 243-257.

Von Gosen, W.; Buggisch, W.; Prozzi, C. 2009. Provenance and geotectonic setting of Late Proterozoic-Early Cambrian metasediments in the Sierras de Córdoba and Guasayán (western Argentina): a geochemical approach. Neues Jahrbuch für Geologie und Paläontologie Abhandlungen 251 (3): 257-284.

Von Gosen, W.; Prozzi, C. 2009. Late Proterozoic to Early Cambrian sedimentation and magmatism at the western Gondwana margin: Metasedimentary rocks in the Sierras Norte de Córdoba (Argentina): Neues Jahrbuch für Geologie und Paläontologie, Abhandlungen 253 (1): 79-101.

Von Gosen, W.; McClelland, W.C.; Loske, W.; Martínez, J.C.; Prozzi, C. 2014. Geochronology of igneous rocks in the Sierra Norte de Córdoba (Argentina): Implications for the Pampean evolution at the western Gondwana margin. Lithosphere 6: 277-300.

Whitney, D.L.; Evans, B.W. 2010. Abbreviations for names of rock-forming minerals. American Mineralogy 95: 185-187.

Willner, A.P. 1990. División tectonometamórfica del basamento del noroeste Argentino. *In* El Ciclo Pampeano en el Noroeste Argentino (Aceñolaza, F.G.; Miller, H.; Toselli, A.J.; editors). Universidad Nacional de Tucumán, Serie Correlación Geológica 4: 113-159. Tucumán.

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