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Geochemistry of Neoproterozoic-Cambrian metasedimentary rocks of the Caucete Group, Sierra de Pie de Palo, Argentina: Implications for their provenance

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ABSTRACT

The Caucete Group is a low-grade metasedimentary sequence of probable late Neoproterozoic-Cambrian age. It is exposed on the western flank of the Sierra de Pie de Palo, a basement block of the Cuyania terrane from western Argentina. The geochemical composition (major, trace and rare-earth elements, and Sm–Nd isotopes) of the El Quemado, La Paz, El Desecho, and Angacos formations (Caucete Group) was used to characterize the sedimentary provenance. We recognized two types of sources: A felsic source (crustal signature) and another mafic source with juvenile signature. Provenance is interpreted to be the mixing between Paleoproterozoic felsic rocks and Mesoproterozoic–Neoproterozoic juvenile rocks sources. This is supported by previous geochronological studies. The Cuyania basement is interpreted to be the Mesoproterozoic and Neoproterozoic juvenile component defined in the Caucete Group (e.g.: ophiolite assemblage of Sierra de Pie de Palo). The Cuyania basement is also considered to be the felsic source (paragneisses and meta-greywackes of the Pie de Palo Complex). We do not consider Gondwana as a provenance source based on the discrepancies in the Sm–Nd isotopic signatures and the detrital zircon provenance ages between the Caucete Group and the surrounding units that are considered to be autochthonous to the southern margin of Gondwana. The Caucete Group Laurentian Sm–Nd isotopic signature suggests that this sector could have been part of the source area. Hence an allochthonous origin for the Caucete Group (Cuyania terrane), derived from southern Laurentia, is supported for the geochemical results presented in this contribution.

1. Introduction

The Caucete Group (Borrello, 1969) is a low-grade metasedimentary sequence composed by unfossiliferous siliciclastic and carbonate rocks strongly affected by deformation and metamorphism during the Ordovician Famatinian orogeny (Ramos et al., 1998). This sequence of probable late Neoproterozoic-Cambrian age is exposed on the western flank of the Sierra de Pie de Palo, Western Sierras Pampeanas of Argentina (Fig. 1). The Caucete Group is the cover sequence on Cuyania (Ramos et al., 1998; Ramos, 2004; Naipauer et al., 2010), a composite terrane that includes the Precordillera (Ramos et al., 1986; Astini et al., 1995) and the Pie de Palo (Ramos et al., 1998; Ramos, 2004) terranes (Fig. 1a). Cuyania is commonly interpreted to be a continental crustal fragment allochthonous to the Gondwana margin and drifted from Laurentia during the early Paleozoic (e.g. Dalla Salda et al., 1992; Thomas and Astini, 1996; Dalziel, 1997; Ramos et al., 1998). Some authors although propose a para-autochthonous origin (Gondwanan) for the Cuyania terrane emplaced to its present position by a strike-slip displacement from the southern sector of Gondwana during the early Paleozoic (Baldis et al., 1989; Aceñolaza et al., 2002; Finney et al., 2005; Finney, 2007). Moreover, other hypothesis also suggests a possible autochthonous origin for the Sierra de Pie de Palo as part of the proto-Andean margin of Gondwana (Galindo et al., 2004; Mulcahy et al., 2007).

Recent detrital zircon U–Pb isotopes (LA-ICP-MS) geochronological analysis from the Caucete Group shows a clear provenance from Laurentian Mesoproterozoic igneous and metamorphic rocks (Naipauer et al., 2010). Geochemical studies on (meta-) sedimentary rocks provide information about the chemical composition of the sediments source, and they may also help to constrain the tectonic setting of the depositional basins (McLennan et al., 1990, 1993, 1995; McLennan and Taylor, 1991; Zimmermann, 2005). New geochemical

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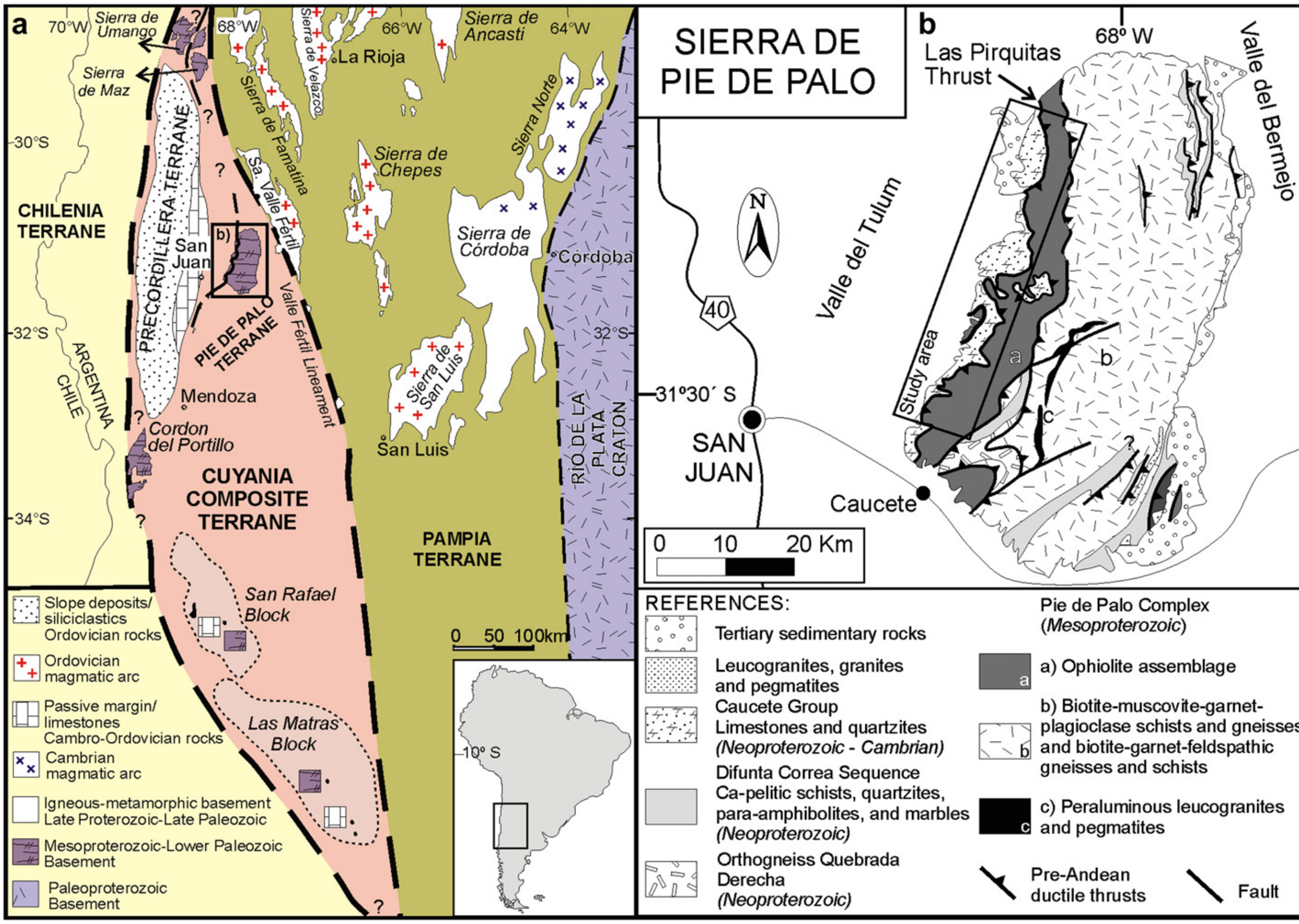

Fig. 1. (a) Regional map of the Cuyania composite terrane (Precordillera and Pie de Palo terranes; Ramos et al., 1998). Ordovician magmatic arc and Pampean basement after Sato et al. (2000, 2004). Rio de la Plata craton after Rapela et al. (2007). (b) Geologic map of the Sierra de Pie de Palo (Ramos and Vujovich, 2000; Baldo et al., 2006; Naipauer et al., 2010).

data, presented here (major, trace and rare-earth elements, and Nd isotopes) allowed us to decipher the sedimentary provenance of the Caucete basin and to compare it with previous studies of neighboring rocks of similar age. A possible provenance from Gondwana or Laurentia was evaluated to better understand the geotectonic evolution of the Cuyania terrane in late Neoproterozoic-Cambrian and its relationship (allochthonous, parautochthonous or autochthonous) with the proto-Andean margin of Gondwana.

2. Gelogical setting and stratigraphy

The Sierra de Pie de Palo is one of the westernmost ranges of the Sierras Pampeanas and is located immediately to the east of the Argentine Precordillera in the San Juan province (Fig. 1a). This range is part of the broken Andean foreland of western and central Argentina originated in response to the Andean orogeny (Ramos et al., 2002; and references therein). Mesoproterozoic rocks are the largest outcrops in the Sierra de Pie de Palo, which consists of medium- to high-grade metamorphic rocks referred to as the Pie de Palo Complex (Ramos and Vujovich, 2000). Neoproterozoic rocks include the Quebrada Derecha orthogneiss (Baldo et al., 2006) cropping out in the south western part of Sierra de Pie de Palo, and the Difunta Correa metasedimentary sequence (Baldo et al., 1998) (Fig. 1b). The late Neoproterozoic to Cambrian metasedimentary Caucete Group (Naipauer et al., 2010) is recognized all along the western flank of the range (Fig. 1b). Fig. 2 summarizes the Sierra de Pie de Palo stratigraphy, outcrop relationships, rock types and ages of the different basement units in an integrated lithostratigraphic column. The contacts between the metamorphic units are controlled by early Paleozoic structures, characterized by an imbricate ductile thrust system with dominant top to west strike sense (Ramos et al., 1998; Ramos and Vujovich, 2000). One of the most outstanding structures is the Las Pirquitas thrust (Fig. 1b) that juxtaposes the Pie de Palo Complex with the Caucete Group (Ramos et al., 1996).

Several authors have extensively described the stratigraphy, lithology and ages of the Caucete Group (Borrello, 1969; Vujovich, 2003; Naipauer et al., 2005, 2010). It comprises of four metamorphic units: the El Quemado, La Paz, El Desecho and Angacos formations (Fig. 2). Two main lithological compositions are recognized, El Quemado and La Paz formations of siliciclastic composition and El Desecho and Angacos formations of carbonate composition.

The depositional age of the sequence is unclear due to the lack of diagnostic fossils, uncertain stratigraphic relationships, penetrative deformation and greenschist facies metamorphism (Ramos and Vujovich, 2000). Maximum depositional ages, based upon detrital zircon dating, were recently defined ca. 550 Ma for the El Quemado Formation and ca. 530 Ma for the El Desecho Formation (Naipauer et al., 2010). An early Paleozoic age was suggested by isotopic studies ($^{87}Sr/^{86}Sr$, C and O) for the Angacos Formation (Linares et al., 1982; Sial et al., 2001; Galindo et al., 2004; Naipauer et al., 2005).

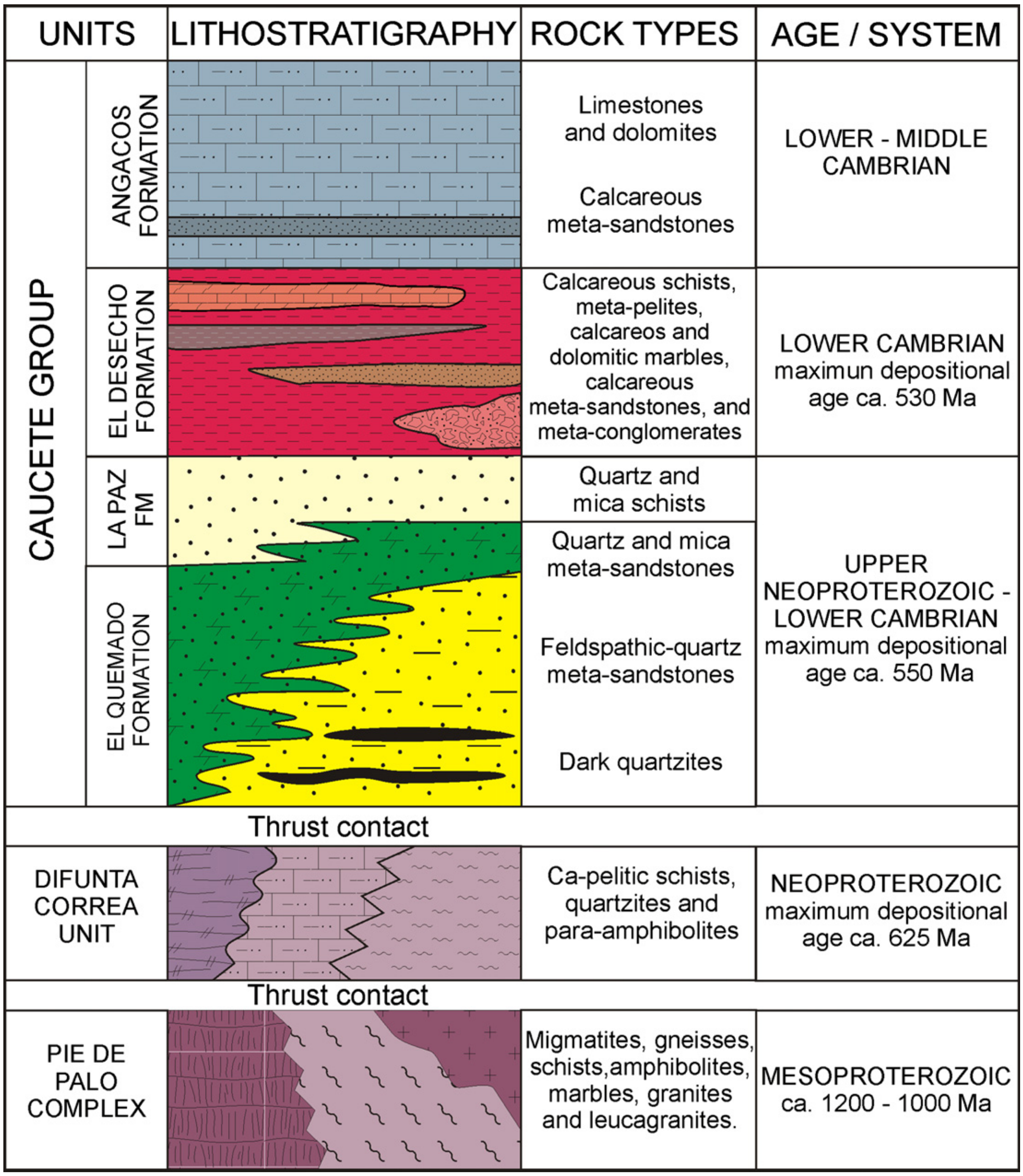

Fig. 2. Integrated lithostratigraphic column-chart of Grenville basement and Neoproterozoic to Cambrian metasedimentary units on the western side of Sierra de Pie de Palo (based on Baldo et al., 1998; Vujovich, 2003; Vujovich et al., 2004; Rapela et al., 2005).

Lithology, isotopic composition, and detrital zircon ages, allows to compare the carbonate formations (El Desecho and Angacos) of the Caucete Group with the sedimentary cover of the Precordillera terrane (Ramos et al., 1998; Ramos, 2004), as part of the same Cambro-Ordovician platform (Galindo et al., 2004; Naipauer et al., 2005, 2010). However, the origin of the siliciclastic, El Quemado and La Paz formations, and the correlation with the unmetamorphosed Precordillera sequences is still matter of debate (Naipauer et al., 2010).

Previous geochemical studies of the Caucete Group are scarce. Vujovich (2003) presented for the first time geochemical analyses of the siliciclastic sediments of the El Quemado and La Paz formations, and compared them with meta-greywacke and metaigneous rocks of the Pie de Palo Complex. Data showed that the deposition of the El Quemado Formation occurred in an intrarift or platform tectonic setting. El Quemado and La Paz formations La/Sc, Th/Sc, and Th/Cr ratios are consistent with orthogneisses and meta-greywackes of the Pie de Palo Complex (Vujovich, 2003).

Naipauer et al. (2005) presented the first T_{DM} model ages for the Angacos Formation, between 1.66 and 1.40 Ga, compared with the La Laja Formation (ca. 1.70–1.31 Ma) in the eastern Precordillera of the San Juan province (T_{DM} ages recalculated with DePaolo, 1981).

The zircon U–Pb (LA-ICP-MS) data of the Caucete Group, presented by Naipauer et al. (2010), allowed us to propose four different provenance areas: (1) an area supplying restricted detrital zircons of metamorphic origin, of ca. 1600 Ma; (2) a crystalline basement, the main source area, dominated by early Mesoproterozoic igneous rocks at ca. 1450–1360 Ma; (3) younger Mesoproterozoic, Grenville-age (ca. 1290–1000 Ma) medium- to high-grade metamorphic rocks and subordinate igneous rocks; and (4) Neoproterozoic-Cambrian (ca. 700–530 Ma) igneous rocks.

Table 1
Samples analyzed for major, trace and rare-earth elements: location, stratigraphic units, major minerals and rock type. Mineral abbreviations after Kretz (1983).

Samples	Location	Major mineral composition	Rock type
El Quemado Formation			
QGM1	Qda. Grande del Molle	Qtz, Kfs, Plag, Ms, Zrn, Op	Meta-sandstone Qtz-Ms-Kfs
QLPcz2	Qda. La Petaca	Qtz, Kfs, Plag, Ms, Zrn, Mo, Op	Meta-sandstone Qtz-Kfs-Ms
VVL41[a]	Qda. El Gato	Qtz, Kfs, Ms, Zrn, Op	Feldspathic-quartz schist
VVL45A[a]	Qda. La Petaca	Qtz, Kfs, Ms, Zrn, Op	Feldspathic-quartz schist
VVL47[a]	Qda. Grande del Molle	Qtz, Kfs, Ms, Bt, Zrn, Op	Schist Qtz-Ms-Bt
VVL56[a]	Qda. Grande del Molle	Qtz, Kfs, Ms, Zrn, Op	Qtz milonite
VVL67[a]	Qda. Las Pirquitas	Qtz, Kfs, Ms, Zrn, Op	Feldspathic-quartz schist
VVL68[a]	Qda. Las Pirquitas	Qtz, Kfs, Ms, Bt, Zrn, Op	Feldspathic-quartz schist
La Paz Formation			
M3	Qda. Grande del Molle	Qtz, Kfs, Plag, Ms, Grt, Zrn, Op	Meta-sandstone Qtz-Alb-Ms-Grt
M5	Qda. La Paz	Qtz, Plag, Ms, Grt, Zrn, Mo	Meta-sandstone Qtz-Alb-Ms-Grt
M6	Qda. La Paz	Qtz, Plag, Ms, Grt, Zrn, Mo	Metapelite
PP500	Lomas Bayas area	Qtz, Plag, Ms, Grt, Zrn, Ca, Op	Meta-sandstone Qtz-Alb-Ms-Grt
PP503	Lomas Bayas area	Plag, Ms, Grt, Qtz, Zrn, Op	Meta-sandstone Alb-Ms-Grt-Qtz
El Desecho Formation			
M 8	La Olla area	Qtz, Ca, Kfs, Plag, Zrn, Mo, Op	Calcareous meta-sandstone
M 11	La Olla area	–	Metapelite
Angacos Formation			
QLli1	Qda. La Lichona	Qtz, Ca, Kfs, Zrn, Mo, Op	Calcareous meta-sandstone

Qda.: *Quebrada* (Creek).
[a] Samples from Vujovich (2003).

Table 2
Locations (GPS coordinates) and rock types of Caucete Group samples for Sm–Nd analyses.

Samples	Location	Lat. (S)	Long. (W)	Rock type
El Quemado Formation				
QEG2	Qda. El Gato	31° 26′ 21″	68° 11′ 15″	Meta-sandstone Qtz-Ms-Kfs
QM3	Qda. Grande del Molle	31° 22′ 59″	68° 08′ 08″	Meta-sandstone Qtz-Kfs-Ms
LB2	Lomas Bayas area	31° 18′ 16″	68° 09′ 10″	Meta-sandstone Qtz-Kfs
M4	South Qda. El Quemado	31° 21′ 19″	68° 10′ 02″	Meta-sandstone Qtz-Kfs-Ms
CFN1	San Ceferino area	31° 34′ 01″	68° 17′ 32″	Meta-sandstone Qtz-Kfs-Ms
M7	Qda. Pecán	31° 26′ 16″	68° 11′ 04″	Dark quartzite
La Paz Formation				
M1	Qda. Grande del Molle	32° 22′ 23″	68° 09′ 31″	Meta-sandstone Qtz-Bt
M3	South Qda. El Quemado	31° 21′ 19″	68° 10′ 02″	Meta-sandstone Qtz-Alb-Ms-Gtr
M5	North Qda. Las Pirquitas	31° 20′ 20″	68° 09′ 17″	Meta-sandstone Qtz-Alb-Ms-Gtr
M6	North Qda. Las Pirquitas	31° 20′ 20″	68° 09′ 17″	Quartz-micaceous schist
QGY3	Qda. Guayaupas	31° 13′ 36″	68° 04′ 12″	Meta-sandstone Qtz-Alb-Ms-Gtr
QAC4	Qda. Agua del Conejo	31° 07′ 21″	68° 04′ 26″	Quartz-micaceous schist
El Desecho Formation				
QEQ4	Qda. El Quemado	31° 21′ 18″	68° 09′ 22″	Dolimitic marble
M8	La Olla area	–	–	Calcareous meta-sandstone
M9	La Olla area	–	–	Calcareous meta-sandstone
M11	Qda. Pecán	31° 26′ 20″	68° 10′ 45″	Calcareous schist
Angacos Formation				
CaA1[a]	Puntilla Blanca quarry	31° 26′ 51″	68° 11′ 43″	Marble
QLP2[a]	Qda. La Petaca	31° 27′ 18″	68° 10′ 38″	Calcareous meta-sandstone
QEG8[a]	Qda. del Gato	31° 26′ 56″	68° 10′ 27″	Calcareous meta-sandstone
QEQ1[a]	Qda. El Quemado	31° 20′ 58″	68° 09′ 17″	Marble
QPir1[a]	Qda. Las Pirquitas	31° 20′ 41″	68° 08′ 52″	Marble
QPP1	Qda. Piedras Pintadas	31° 29′ 28″	68° 12′ 54″	Calcareous meta-sandstone
ANG1v	Qda. del Gato	31° 27′ 05″	68° 10′ 56″	Marble
ANG2v	Qda. del Gato	31° 27′ 05″	68° 10′ 56″	Marble
ANG5v	Qda. del Gato	31° 27′ 05″	68° 10′ 56″	Marble
ANG6h	Qda. del Gato	31° 27′ 05″	68° 10′ 56″	Marble

Qda.: *Quebrada* (Creek).
[a] Samples from Naipauer et al. (2005).

3. Samples description and analytical methods

The Caucete Group was sampled on the western flank of the Sierra de Pie de Palo. Sixteen samples for major, trace and rare-earth elements analysis were selected. Two samples QGM1 and QLPcz2 are from the El Quemado Formation. Six samples previously analyzed by Vujovich (2003) of the same unit were also studied (VVL41, VVL45A, VVL47, VVL56, VVL67, and VVL68). Five samples from the La Paz Formation (M3, M5, M6, PP500, and PP503), two samples (M8 and M11) for the El Desecho Formation and one (QLli1) for the Angacos Formation were also analyzed. Sample locations, stratigraphic units, main mineral composition, and rock types are shown in Table 1.

Twenty-one samples of the Caucete Group were analyzed for Sm–Nd. They include six samples of the El Quemado Formation (QEG2, QM3, LB2, M4, CFN1, and M7), six of the La Paz Formation (M1, M3, M5, M6, QGY3, and QAC4), four of the El Desecho Formation (QEQ4; M8, M9, and M11), and five of the Angacos Formation (ANG1v, ANG2v, ANG5v, ANG6h, and QPP1). Data from five samples of the Angacos Formation of Naipauer et al. (2005) (CaA1, QEQ1, QPir1, QLP2, and QEG8) are included. Location of samples (GPS coordinates) and lithology of the rocks analyzed are shown in Table 2.

All samples were washed with distilled water and pulverized in a mill at the Centro de Investigaciones Geológicas from the Universidad Nacional de La Plata, Argentina. Geochemical analyses (major elements) of two samples (QLPcz2 and QGM1) were obtained by X-ray fluorescence at the University of Johannesburg, South Africa. The trace and rare-earth element analyses were carried out at ACME Labs, Canada, by fusion ICP-MS. Eight samples (M3, M5, M6, PP500, PP503, M8, M11, and QLli1) were analyzed for major elements by ICP (Inductively Coupled Plasma) and for trace elements by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) at ACTLABS Co. Laboratories, Canada.

Whole rock Sm–Nd analyses were carried out at the Laboratório de Geologia Isotópica, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brasil. The whole-rocks samples were entirely dissolved in Teflon containers using a mixture of HNO_3, HF and HCl-$_6$N after the addition of a combined spike of $^{149}Sm/^{150}Nd$. Chromatography columns with cationic resin AG-50w-X8 (200–400 mesh) were used for separation of REE; subsequently Nd and Sm were separated using anionic resin HDEHP LN-B50 (100–200 μm). Each sample was dried and was loaded with H_3PO_4 0.25 N onto a Ta-Re filament. The isotopic ratios were measured with a VG mass-spectrometer sector 54 with multicollector (TIMS). Nd ratios were normalized to $^{146}Nd/^{144}Nd = 0.72190$ and calculated assuming $^{147}Sm/^{144}Nd_{(mantle)} = 0.222$, $^{143}Nd/^{144}Nd_{(mantle)} = 0.513114$,

Table 3
Major oxides (SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O and K_2O) and minor oxides (MnO, TiO_2 and P_2O_5) of the Caucete Group samples.

Units (N° sample)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (T) (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	P_2O_5 (%)	LOI (%)	Total (%)
El Quemado Formation												
QGM1[a]	90.20	2.82	0.62	0.01	0.06	0.07	2.15	1.80	0.20	0.02	0.49	98.43
QLPcz2[a]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.34	n.d.
VVL41[b]	85.07	8.50	0.60	n.d.	0.24	0.07	0.16	5.11	0.54	0.01	n.d.	100.30
VVL45A[b]	79.99	9.67	1.60	0.01	0.81	0.06	0.30	4.96	0.37	0.02	n.d.	97.78
VVL473[b]	85.22	4.54	1.59	0.02	3.29	2.17	0.03	1.87	0.23	0.09	n.d.	99.05
VVL56[b]	88.03	5.40	0.85	0.01	0.28	0.08	0.04	2.60	0.11	0.03	n.d.	97.43
VVL67[b]	85.90	7.40	0.50	n.d.	0.25	0.04	0.14	4.21	0.17	0.01	n.d.	98.62
VVL68[b]	82.90	8.10	2.38	0.01	0.98	0.10	0.54	2.73	1.59	0.02	n.d.	99.35
La Paz Formation												
M3[c]	61.77	18.3	6.81	0.12	1.87	1.26	2.32	3.38	0.94	0.2	2.8	99.75
M5[c]	71.23	13.47	4.42	0.08	1.3	1.98	3.71	1.93	0.67	0.13	1.2	100.1
M6[c]	67.60	13.76	6.22	0.14	1.62	2.27	2.86	2.38	1.19	0.27	1.69	100
PP500[c]	67.36	15.03	5.11	0.08	1.43	1.23	2.47	2.64	0.67	0.11	2.94	99.07
PP503[c]	51.24	21.14	10.79	0.12	2.79	1.57	4.75	2.24	1.15	0.02	3.27	99.09
El Desecho Formation												
M8[c]	68.94	0.97	1.63	0.29	4.7	9.34	0.22	0.55	0.05	0.12	12.97	99.78
M11[c]	50.90	14.92	8.05	0.02	4.45	5.09	0.23	7.41	0.90	0.19	7.52	99.69
Angacos Formation												
QLli1[c]	57.27	1.86	0.75	0.03	0.34	21.48	0.05	0.51	0.22	0.06	17.63	100.2

n.d.: not determined.
[a] Measures by X-ray fluorescence at the University of Johannesburg, South Africa.
[b] Published data from Vujovich (2003), measured by X-ray fluorescence (XRF).
[c] Measured by ICP (inductively coupled plasma) at ACTLABS Co. Laboratories, Canada.

$^{147}Sm/^{144}Nd_{(CHUR)} = 0.1967$, and $^{43}Nd/^{144}Nd_{(CHUR)} = 0.512638$. Measurements for the La Jolla standard gave $^{143}Nd/^{144}Nd = 0.511859 \pm 0.000010$. T_{DM} ages were calculated with DePaolo (1981) and recalculated from original sources when needed.

4. Geochemical results

The aim of this contribution was to apply geochemistry to characterize the sampled sediments provenance area using immobile trace and rare-earth elements (REE), and Nd isotopes (Taylor and McLennan, 1985; Bhatia and Crook, 1986; McLennan et al., 2003). Mobile elements such as Si, Na, K, Ca, Mg, Fe, and Mn and trace, Rb and Sr were not included because they can undergo chemical disturbances (in abundance, ratios, etc.) during weathering, erosion, sediment transport (sorting), deposition, and diagenesis (Nesbitt and Young, 1982; McLennan and Taylor, 1991; McLennan et al., 2003; and reference therein). Further, the Caucete Group was metamorphosed up to greenschist facies and a protracted history of strong deformation that may significantly also affect the mobility of elements. The relatively immobile elements (Al, Ti, Zr, Hf, Nb, Sc, Cr, Ni, V, Co, Th, and REE) are considered to be transported from the source area to the basin preserving the geochemical characteristics of the source rocks, thus they can be considered as reliable provenance indicators (McCulloch and Wasserburg, 1978; Taylor and McLennan, 1985; Bhatia and Crook, 1986; McLennan, 1989; McLennan et al., 2003). Furthermore, the application of the Sm–Nd isotopic system to a sedimentary rock is widely used as another provenance indicator (McLennan et al., 1990, 2003; McLennan, 1993). Nd isotopic signatures can provide an average of the various sources from which sediments were derived (McLennan et al., 1993, 2003; and references therein).

4.1. Major element geochemistry

Analytical data for the major oxides [SiO_2, Al_2O_3, Fe_2O_3 (T), MnO, MgO, CaO, Na_2O, K_2O, TiO_2, and P_2O_5] of the analyzed samples and from Vujovich (2003) are given in Table 3. In the El Quemado Formation the SiO_2 content varies between 90 and 85%, higher to the average composition of the upper continental crust (UCC), 66% according to Taylor and McLennan (1985). The content of Al_2O_3 (9.5–2.9%), Fe_2O_3 (2.4–0.5%), CaO (2.2–0.04%), and Na_2O (2.15–0.03%) showing low concentrations with respect to UCC, and the contents of K_2O (5.1–1.8%) and TiO_2 (1.6–0.1%) are similar in the range of the UCC (see average content of UCC in Taylor and McLennan, 1985). The percentages of the major oxides are representative of the mineral composition of the El Quemado Formation samples studied (quartz meta-sandstones and feldspathic-quartz schists).

The percentage of SiO_2 in La Paz Formation decreases significantly to values of 71% and 51%, with respect to El Quemado Formation, but these contents are in better accordance with the average composition of the UCC from Taylor and McLennan (1985). The content of Al_2O_3 (21.1–13.5%), Fe_2O_3 (10.8–4.4%), MgO (2.8–1.3%), Na_2O (4.75–2.3%), K_2O (3.4–1.9%), and TiO_2 (1.2–0.7%) are similar to the UCC, whereas the percentages of CaO (2.3–1.2%) are lower to the UCC. The increase of Al, Fe, K, and Na with respect to El Quemado Formation are probably representing a higher abundance of muscovite, albite, and garnet in the La Paz Formation.

The rocks analyzed in the El Desecho Formation have SiO_2 content of 69% and 51%, similar to the La Paz Formation. However, the CaO (9.3% and 5.1%) is higher with respect to other units and the UCC, probably because the carbonate matrix observed in these rocks. In the metapelite (M11) the increase of Al, Fe, and K, along with a decrease in the content of SiO_2, is in agreement with the decrease of quartz and the clay fraction increment.

The percentages of major oxides of the Angacos Formation (QLli1 sample) are characterized by a low content of SiO_2 (57%), Al_2O_3 (1.9%), Fe_2O_3 (0.75%), MgO (0.3%), Na_2O (0.05%), K_2O (0.5%), and TiO_2 (0.2%) with respect to the other units and the UCC, but present a higher percentage of carbonates, 21.5% of CaO, coherent with the lithology of the sample (meta-calcareous sandstone) with high content of a carbonate matrix and quartz grains.

4.2. Trace element geochemistry

Table 4 shows the trace elements of the Caucete Group samples analyzed. The Th/Sc ratio is considered a robust provenance indicator to differentiate mafic *vs.* felsic sources (Taylor and McLennan, 1985; McLennan et al., 1990). Detritus from felsic rocks of the UCC have an average ratio equal to or greater than 0.79, while values less than 0.6 suggest mafic and ultramafic components (McLennan et al., 1990). Cr, V, Ni, and Sc are concentrated in mafic rocks, and therefore they are useful to evaluate the input of a mafic/ultramafic source. It should be noted that the Zr/Sc and Zr/Th ratios were assessed for their importance in quantifying the degree of recycling of sediments, because the concentration of Zr is directly related to the content of zircon accumulation in the sediments, which in turn evidences the degree of recycling (McLennan et al., 1990). Fig. 3 shows the Th/Sc and Zr/Sc ratios for rocks of the Caucete Group. The diagram represents the composition of the source and the extent of recycling or concentration of Zr in sediments.

The Th/Sc ratios of samples of the El Quemado Formation (Table 4) are in a range between 4.37 and 0.34 and many of the ratios are above 0.79 (Fig. 3), indicating a felsic sources similar than UCC (samples VVL41, QLPcz2. VVL67, and QGM1). However, some ratios lower than 0.6, suggest a contribution from sources related to less evolved rocks of mafic and/or ultramafic composition (samples VVL45A, VVL47 and VVL68) (Fig. 3). It should be pointed that no sample of the El Quemado Formation are enriched with Sc, Cr, and V (Table 4) with respect to the average of the UCC which contents

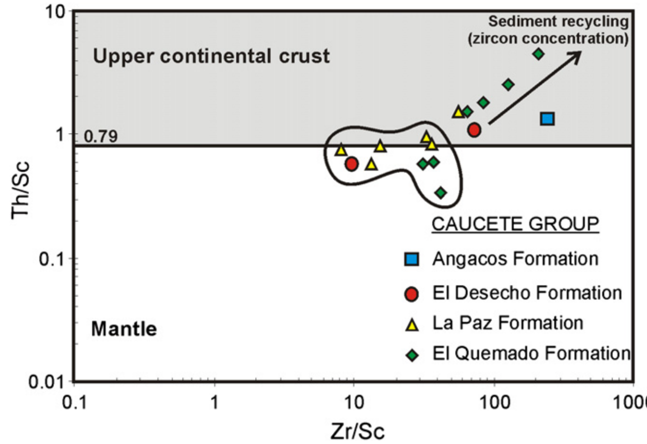

Fig. 3. Th/Sc and Zr/Sc ratio diagram for rocks of the Caucete Group. In this diagram one can visualize the composition of the sources and the extent of recycling or concentration of Zr in sediments, associated with the abundance of heavy minerals, particularly zircon (after McLennan et al., 1990).

Table 4
Trace elements for samples of the Caucete Group.

Units	El Quemado								La Paz					El Desecho		Angacos
	QLPcz2[a]	QGM1[a]	VVL41[b]	VVL45A[b]	VVL47[b]	VVL56[b]	VVL67[b]	VVL68[b]	M 3[c]	M 5[c]	M 6[c]	PP500[c]	PP503[c]	M 8[c]	M 11[c]	QLIi1[c]
Sc	2.7	1.3	1	3	8	n.d.	1	7	17	11	15	14	25	1	18	1
V	31.9	17.9	22	34	39	13	19	68	97	54	79	79	111	7	117	10
Ba	420	430	565	594	214	309	625	534	767	564	500	523	721	60	451	54
Sr	b.d.l.	b.d.l.	52	66	12	14	46	78	146	197	192	204	192	77	23	91
Y	6	1.7	10.8	8.9	24.39	2.3	4.3	5.19	47	42	79	36	64	18	44	18
Zr	355.2	86.4	215	117	345	69	87	228	269	380	866	194	212	75	178	249
Cr	21	19	21	19	17	25	39	126	80	30	60	50	70	20	60	30
Co	18	32	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	16	8	14	12	24	b.d.l.	16	b.d.l.
Ni	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Cu	3.1	2.7	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	40	20	20	40	20	b.d.l.	20	10
Zn	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	110	70	100	80	170	b.d.l.	80	b.d.l.
Ga	5.1	4	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	27	18	22	19	26	2	25	3
Rb	44	29	70	56.30	30.10	40.20	39.90	39.30	125	72	114	82	79	8	146	13
Nb	12.9	4.4	4.8	1.7	4.1	2	2.2	14.1	18	12	114	199	26	5	37	5
Cs	b.d.l.	b.d.l.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.1	2.6	2.2	1.7	1.9	b.d.l.	7.9	b.d.l.
La	17	4.7	15.5	7.6	7.7	2.9	8.7	2.9	49	36.5	64.7	31.6	68.4	8.9	47.8	8.2
Ce	38	11	33.1	16.1	17.7	10.4	16.5	6	105	82.6	141	70.1	139	24.2	105	23.7
Pr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	14	10.9	18.7	9.28	19	2.3	12.3	2.56
Nd	n.d.	n.d.	16	8.6	8.9	6.7	6.5	4.1	49.2	40.5	70.7	34.4	68.3	8.8	46.2	10.7
Sm	3.3	1	2.96	1.77	1.99	1.18	0.93	0.85	10.1	9	16	7.3	14.2	2.2	9.7	2.6
Eu	0.6	0.2	0.53	0.53	0.39	0.27	0.27	0.25	2.02	1.88	2.72	1.51	2.49	0.53	1.91	0.75
Gd	n.d.	n.d.	2.45	1.61	2.51	0.98	0.68	0.77	9.5	8.3	15.3	6.7	12.6	2.5	8.8	2.8
Tb	b.d.l.	b.d.l.	0.34	0.25	0.49	0.1	0.09	0.13	1.6	1.3	2.4	1.1	2	0.5	1.4	0.5
Dy	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8.5	7.2	13.5	6.1	11.6	2.8	7.9	2.8
Ho	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.7	1.5	2.7	1.2	2.3	0.6	1.6	0.6
Er	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.9	4.3	7.9	3.3	6.7	1.8	4.6	1.8
Tm	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.77	0.68	1.22	0.52	1.04	0.26	0.67	0.27
Yb	2	0.8	1.33	1.06	3.18	0.21	0.27	0.86	4.9	4.4	7.9	3.5	6.6	1.7	4.2	1.8
Lu	0.36	0.13	0.20	0.16	0.48	0.03	0.04	0.15	0.73	0.66	1.15	0.5	0.93	0.23	0.59	0.28
Hf	13	4	4.20	2.5	7	1.8	1.3	4.4	8.4	11.1	24.2	6	6.6	2.2	5.5	6.5
Ta	1.4	2.1	0.6	0.2	0.5	0.3	0.3	0.7	3.9	3.2	169	354	4.5	2.9	34.6	1
Pb	4.5	5.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	19	28	14	18	21	b.d.l.	b.d.l.	b.d.l.
Th	6.7	1.5	4.4	1.8	2.7	2.4	1.8	4.1	13.8	10.6	22.6	8	19.1	1.1	10.6	1.3
U	2	b.d.l.	0.9	0.3	0.5	0.2	0.2	0.8	3.9	2.8	7.2	4.9	5.8	0.4	2	2.3
Th/Sc	2.48	1.5	4.37	0.59	0.34	0	1.78	0.58	0.81	0.96	1.51	0.57	0.76	1.1	0.59	1.3
Zr/Sc	131.5	66.5	215	39	43.125	0	87	32.6	15.8	34.5	57.7	13.8	8.5	75	9.9	249
La/Th	2.54	3.13	3.52	4.22	2.85	1.21	4.83	0.71	3.52	3.44	2.86	3.95	3.58	3.09	4.51	6.35
La/Sc	6.3	3.61	15.49	2.52	0.96	0	8.73	0.41	2.88	3.32	4.31	2.26	2.74	8.9	2.65	8.2
ΣETR	61.36	18.33	72.4	37.6	43.4	22.8	34	16	261.92	209.72	365.89	177.11	355.16	57.32	252.67	56.06

n.d.: not determined. b.d.l.: below detection limit.
[a] Measures by fusion ICP-MS (inductively coupled plasma mass spectrometry) at ACME Labs, Canada.
[b] Published data from Vujovich (2003), ICP-MS at ACTLABS Co. Laboratories, Canada.
[c] Measures by ICP-MS at ACTLABS Co. Laboratories, Canada.

are, Sc = 13.6, Cr = 83, and V = 107, according to McLennan (2001). One sample (VVL68) has Cr content higher (126 ppm) and it has also a low Th/Sc ratio (0.58), this sample probably shows contribution from a mafic/ultramafic source.

The Th/Sc ratios of the La Paz Formation analyzed rocks, varies between 1.51 and 0.57, nearly all these ratios (samples M3, M5, and M6) are above the average for the UCC (0.79; McLennan et al., 1990) and are probably derived from felsic sources. Two samples, PP500 and PP503, whose ratios are 0.57 and 0.76 respectively, are under the average for UCC, suggesting a probable contribution from less evolved rocks (Fig. 3). Cr content of the samples is between 80 and 30 ppm, all below the average for continental crust (83 ppm; McLennan, 2001). One sample PP503 is enriched in Sc (25 ppm), V (111 ppm), and Co (24 ppm) with respect to the averages of UCC (Sc = 13.6, V = 107, Co = 17 ppm; according to McLennan, 2001). Also, the Zr/Sc ratio from this sample (8.5) is lower than 13.13 of the PAAS (Post-Archean Australian Average Shale; Taylor and McLennan, 1985). These ratios means that recycling was not significant and contribution from sources geochemically less evolved than the UCC as mafic rocks could be considered.

Sample M11 from El Desecho Formation has a low Th/Sc ratio (0.59) and is enriched in Sc (18 ppm), V (117 ppm), and Co (18 ppm) with respect to the averages of UCC (McLennan, 2001). The Zr/Sc ratio is 9.9, similar to the PP503 sample, and lower than the PAAS (13.13, Taylor and McLennan, 1985). The composition of this metapelite suggests a likely contribution from a mafic source and geochemically less evolved than the UCC. In contrast, sample M8 from the same unit has Th/Sc (1.1) and Zr/Sc (75) ratios that indicate similar composition than the UCC (Fig. 3). Both samples (M11 and M8) are not enriched in Cr content (60 and 20 ppm respectively) compared to UCC.

The sample QLli1 (Angacos Formation) have a Th/Sc ratio of 1.3 that indicate provenance from a felsic source, the sample has not evidence of a mafic source contribution, i.e. the contents of Sc = 1, V = 7, Cr = 20 ppm are not enriched.

On the other hand, samples VVL41, QLPcz2. VVL67, QGM1 (El Quemado Formation), M6 (La Paz Formation), M8 (El Desecho Formation), and QLli1 (Angacos Formation) present a high Zr/Sc ratio due to high content of Zr, indicating concentration of this element in heavy minerals (zircon). Also, we can interpret that as an evidence of the high grade of sediment recycling including in the Caucete Group (Fig. 3).

4.2.1. Tectonic discrimination

Tectonic discrimination diagrams were created by different authors using trace elements such as Th, Sc, Zr, La, and Hf after Taylor and McLennan (1985), Bhatia and Crook (1986), McLennan et al. (1990), and recent contributions by Bahlburg (1998) and Zimmermann (2005), among others. However, all these authors remark that sedimentary rocks belonging to similar tectonic setting could present different geochemical signatures (McLennan et al., 1990; Bahlburg, 1998). For this reason, the results obtained from these diagrams should be interpreted with caution.

We used the Sc–Th–Zr/10 plot of Bhatia and Crook (1986), amended by McLennan et al. (1990) and Bahlburg (1998), because it can discriminate sediments from passive margin to active continental margin settings. Modern clastic rocks were also included in the database of the diagram by Bahlburg (1998).

Fig. 4 shows the El Quemado Formation samples data. They plot mostly or close to the passive margin or rifted margin field and are similar to recent deep-sea turbidites derived from and deposited at passive margins settings (according McLennan et al., 1990; Bahlburg, 1998). By contrast, samples of La Paz Formation are largely within the field of recent deep-sea turbidites derived from and/or deposited on a continental arc margin (McLennan et al., 1990; Bahlburg, 1998). Two samples are exceptions, located near the field of modern passive margins (Fig. 4). Sample M8 from El Desecho Formation plots very close to the group of samples from the El Quemado Formation while sample M11 plots in the field of continental arc margins close to La Paz Formation samples (Fig. 4). The Angacos Formation sample plots close to the area of recent deep-sea turbidites derived from and deposited on passive margins with a high degree of recycling what is evidenced by the concentration of Zr (McLennan et al., 1990; Bahlburg, 1998) (Fig. 4).

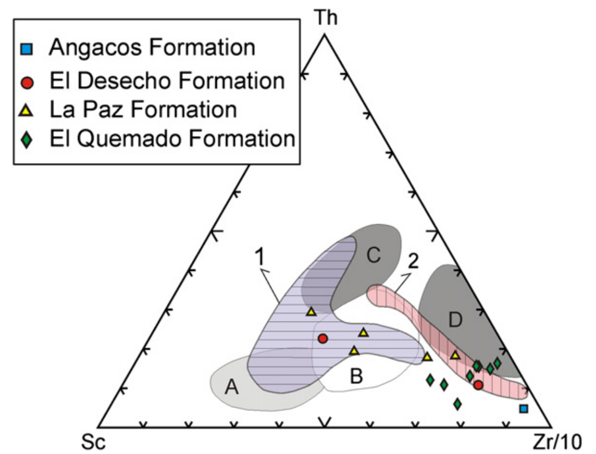

Fig. 4. Sc–Th–Zr/10 diagram of Bhatia and Crook (1986) and Bahlburg (1998). A: oceanic island arc; B: continental island arc; C: active continental margin; D: passive/rifted margins; (1) recent deep-sea turbidites derived from and deposited at a continental arc margin; (2) recent deep-sea turbidites derived from and deposited at a passive margin (data from Bahlburg, 1998).

In summary, the meta-sandstones (El Quemado Formation) and the meta-calcareous sandstones (El Desecho and Angacos formations) plotted principally in the field of passive margin or rifted margin and close to it. The meta-sandstones from the La Paz Formation plotted both in the field of active continental margins and in the field of passive margin or rifted margin. However the interlayering of the La Paz with El Quemado formations and the provenance indicators discussed above suggests that both La Paz and El Quemado formations belong to the same tectonic setting.

4.3. Rare-earth elements

Rare-earth elements (REE) are widely used in studies of provenance of sedimentary rocks because of their insolubility (Taylor and McLennan, 1985; Bhatia and Crook, 1986; among others). Concentration of REE is strongly influenced by grain size; Cullers et al. (1987) found that the concentration of the REE is approximately 20% higher in shales than in sandstones. Evaporite and carbonate rocks have a low REE content usually lower than 10 ppm, although their pattern distribution is generally similar to that of clastic rocks (Taylor and McLennan, 1985). Mineralogy also exerts a control over the concentration of REE; heavy minerals such as zircon, monazite and garnet contribute significantly to the increase in HREE content (Morton, 1991). Also, the presence of a negative pick representing a Eu-anomaly indicates a typical continental crust composition; virtually all post-Archean sedimentary rocks are characterized by Eu depletion (Taylor and McLennan, 1985). However, igneous rocks as MORBs, island-arc basalts and andesites are not characterized by an Eu-anomaly thus sedimentary rocks derived of this sources and/or deposited in fore-arc basins of island arcs do not show Eu depletion (Taylor and McLennan, 1985; McLennan et al., 2003).

The REE abundances in clastic rocks are commonly comparable with respect to NASC (North American shale composite; Gromet

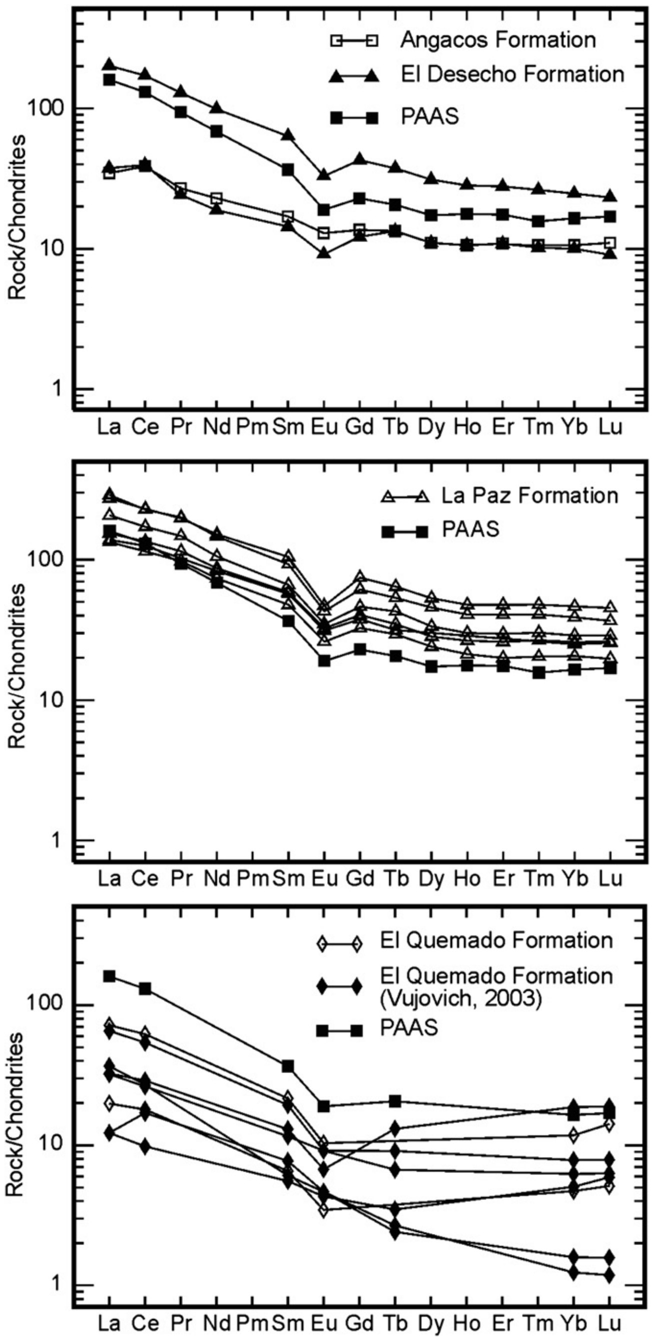

Fig. 5. Chondrite-normalized REE, according to Sun and McDonough (1989), for samples of the Caucete Group and for post-Archean average shale (PAAS, Taylor and McLennan, 1985).

et al., 1984) and also the PAAS (Taylor and McLennan, 1985). In this study PAAS normalized patterns were included in the chondrite-normalized REE spider diagrams (Sun and McDonough, 1989). Analytical results are presented in Table 4 and Fig. 5.

In samples of El Quemado Formation, the REE abundances vary between 72.4 and 18.3 ppm; they are coherent with the ranges defined for sandstones (approximately 25 ppm; Taylor and McLennan, 1985). In the chondrite-normalized REE diagram, the REE content is lower with respect to PAAS, but patterns are similar. They are enriched in LREE with respect to HREE (Fig. 5). Particularly, samples VVL56 and VVL67 are considerably depleted in HREE, probably because these rocks are fine-grained mylonites with high quartz content (more than 85%; Vujovich, 2003). The samples QGM1, QLPcz2, VVL41, VVL47, and VVL56 have a negative Eu-anomaly that allows interpreting a UCC provenance. However, samples VVL45A, VVL67, and VVL68 do not have a strong Eu-anomaly. Particularly sample VVL68 that has the highest Cr concentration (126 ppm) and Th/Sc ratio less than 0.79, indicating the contribution of a depleted source.

The content of REE in the La Paz Formation samples varies between 365.9 and 177.1 ppm. The REE patterns are characterized by LREE enrichment with respect to HREE, showing a subhorizontal array, consistent with their fine grain size (fine and very fine sandstones) and probably their mineralogical composition (muscovite, garnet, and zircon). All samples have an Eu-anomaly indicating a continental crust derivation. In general the REE patterns are similar to PAAS although the La Paz samples are enriched (Fig. 5).

The meta-calcareous sandstones of El Desecho and Angacos formations have low concentrations of REE ($M8 = 57.3$ ppm and $QLli1 = 56.1$ ppm) with respect to UCC, that could be due to the high content of quartz and carbonate in the samples. Sample M11 from a metapelite of El Desecho Formation shows a high content of REE (252.7 ppm), which is consistent with its pelitic composition. The REE patterns of these three samples described are similar to PAAS, enriched in LREE with respect to HREE and have a negative Eu-anomaly (Fig. 5).

4.4. Nd isotopes

The εNd is a measure of the deviation of the $^{143}Nd/^{144}Nd$ ratio in a sample from the expected ratio value in a uniform chondritic reservoir (CHUR) where $\varepsilon Nd = 0$ (DePaolo, 1981). In sedimentary rocks the εNd parameter is considered to be a strong provenance indicator. Positive values of εNd characterize juvenile mantle-derived sources, whereas negative εNd values are associated with rocks from an ancient continental crustal source (McLennan et al., 1990; McLennan, 1995). The El Quemado Formation samples shows $\varepsilon Nd_{(t)}$ ($t = 550$ Ma, considered to represent the maximum depositional age) ranging from +0.93 to −1.13. In the La Paz Formation the $\varepsilon Nd_{(t)}$ ($t = 550$ Ma) is between +0.81 and −2.22. For the El Desecho Formation the $\varepsilon Nd_{(t)}$ ($t = 531$ Ma, maximum depositional age) is between +4.95 and −0.70. The Angacos Formation samples show negative $\varepsilon Nd_{(t)}$ ($t = 520$ Ma, $^{87}Sr/^{86}Sr$ isotopes age) between −0.87 and −3.57 (Table 5).

The model ages (T_{DM}) calculated from Nd isotopes using the classic model of DePaolo (1981) reveals values between 1.66 and 1.05 Ga for the Caucete Group (Table 5), plus an isolated value at ca. 0.63 Ga (QEQ4 sample).

The overall distribution of T_{DM} ages is bimodal, with a peak at ca. 1.20 Ga and a secondary peak at ca. 1.60 Ga (Fig. 6). Analyzing each unit, samples of the El Quemado Formation are characterized by a unimodal distribution and with a maximum ca. 1.20 Ga. In the La Paz Formation T_{DM} ages have a distribution with a peak at approximately 1.10 Ga. The El Desecho Formation yielded similar values; three samples have T_{DM} ages close to 1.20 Ga but a dolomitic marble yielded an isolated age at ca. 0.63 Ga and $\varepsilon Nd_{(t)} + 4.95$ (QEQ4), these values are difficult to interpret because we have no other geochemical data from this sample. The samples for the Angacos Formation showed different T_{DM} ages from those found in previous units, falling in the range between 1.66 and 1.28 Ga. The bimodal distribution is remarkable, with maximum relative probabilities between 1.40 and 1.30 Ga and ca. 1.70–1.60 Ga (Fig. 6).

4.4.1. Implications of the isotopic data

The integrated analysis of $\varepsilon Nd_{(t)}$ and T_{DM} ages showed some differences among units of the Caucete Group. The El Quemado, La

Table 5
Nd isotope data for detrital sediments of the Caucete Group. Age of deposition of the El Quemado (550 Ma), La Paz (550 Ma), and El Desecho (531 Ma) formations are after Naipauer et al. (2010), Angacos Formation age (520 Ma) after Naipauer et al. (2005).

Formation	Age	Sm	Nd	$^{147}Sm/^{144}Nd$	$^{143}Sm/^{144}Nd$	εNd (0)	$\varepsilon Nd_{(t)}$	T_{DM}
El Quemado								
QEG2	550	2.36	13.10	0.10882	0.51232	−6.30	−0.13	1076
QM3	550	1.54	7.51	0.12429	0.51238	−5.11	−0.03	1151
LB2	550	0.74	3.87	0.11638	0.51230	−6.67	−1.03	1180
M4	550	0.85	4.39	0.11668	0.51231	−6.32	−0.70	1157
CFN1	550	2.82	14.39	0.11835	0.51231	−6.43	−0.94	1184
M7	550	1.91	9.59	0.12028	0.51241	−4.44	0.93	1054
La Paz								
M1	550	1.08	5.16	0.12667	0.51240	−4.71	0.21	1146
M3	550	9.04	45.50	0.12009	0.51225	−7.51	−2.13	1286
M5	550	7.88	38.20	0.12477	0.51233	−6.01	−0.97	1229
M6	550	8.72	42.05	0.12539	0.51242	−4.19	0.81	1090
QGY3	550	4.81	36.52	0.07968	0.51210	−10.43	−2.22	1082
QAC4	550	5.82	27.89	0.12608	0.51229	−6.79	−1.83	1308
El Desecho								
QEQ4	531	0.54	12.47	0.02624	0.51230	−6.62	4.95	635
M8	531	1.57	6.59	0.14364	0.51250	−2.68	0.92	1192
M9	531	1.74	7.47	0.14101	0.51249	−2.89	0.88	1174
M11	531	5.98	29.45	0.12282	0.51235	−5.71	−0.70	1180
Angacos								
CaA1[a]	520	0.09	0.38	0.13787	0.51226	−7.48	−3.57	1553
QLP2[a]	520	4.18	17.36	0.14575	0.51229	−6.72	−3.36	1638
QEG8[a]	520	1.96	9.16	0.12929	0.51226	−7.42	−2.94	1405
QEQ1[a]	520	0.71	2.88	0.14934	0.51240	−4.72	−1.58	1504
QPir1[a]	520	0.44	1.74	0.15155	0.51234	−5.75	−2.76	1664
QPP1	520	4.87	22.74	0.12948	0.51233	−5.99	−1.53	1289
ANG1v	520	0.14	0.59	0.14592	0.51240	−4.56	−1.19	1420
ANG2v	520	0.05	0.21	0.13325	0.51227	−7.13	−2.93	1443
ANG5v	520	0.09	0.39	0.13585	0.51237	−5.15	−1.12	1308
ANG6h	520	0.10	0.42	0.13569	0.51239	−4.92	−0.87	1285

Sm and Nd concentration are in ppm. T_{DM} ages were calculated according to DePaolo (1981).
[a] Published data from Naipauer et al. (2005).

Paz and El Desecho formations have a $\varepsilon Nd_{(t)}$ between +4.95 and −2.2 and a unimodal distribution of T_{DM} ages at ca. 1.20 Ga. It is important to note that the T_{DM} age of 0.63 Ga ($\varepsilon Nd_{(t)}$ + 4.95) from El Desecho Formation, is interpreted to represent a juvenile source rock. The Angacos Formation showed negative $\varepsilon Nd_{(t)}$ (between −3.57 and −0.9) and bimodal distribution in the T_{DM} ages. The older Paleoproterozoic peak (ca. 1.70 and 1.60 Ga) and the negative $\varepsilon Nd_{(t)}$ values, suggests that an evolved Paleoproterozoic source contributed in the sediments provenance.

The εNd evolution diagram of the Caucete Group shows a single vertical array at their depositional age (approximately 550–520 Ma) with $\varepsilon Nd_{(t)}$ ranging between approximately +5 and −4, see Fig. 7. These values are between typical upper continental crust (εNd less than −5) and mantle-derived volcanic/plutonic rocks (εNd higher than +3), according to McLennan et al. (1993, 1995). We suggest that there is a significant juvenile component (Neoproterozoic–Mesoproterozoic) in the source rock, but also we cannot rule out an upper continental crust source (Paleoproterozoic), because the sediments reflect a mixture of both source areas. Moreover, we can also consider the $\varepsilon Nd_{(t)}$ and T_{DM} ages of the Caucete Group as representing a Paleoproterozoic/Mesoproterozoic old juvenile crust.

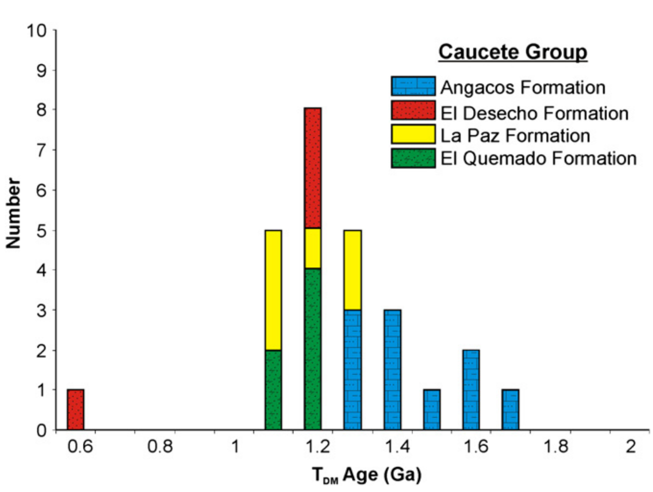

Fig. 6. Histogram of Sm–Nd model ages (T_{DM}) calculated according to DePaolo (1981) for the Caucete Group Formations.

5. Summary of provenance indicators

The analyzed metasedimentary rocks of the Caucete Group showed provenance signatures (particularly Th/Sc and Zr/Sc ratios, REE patterns, and Eu-anomaly), that are compatible with

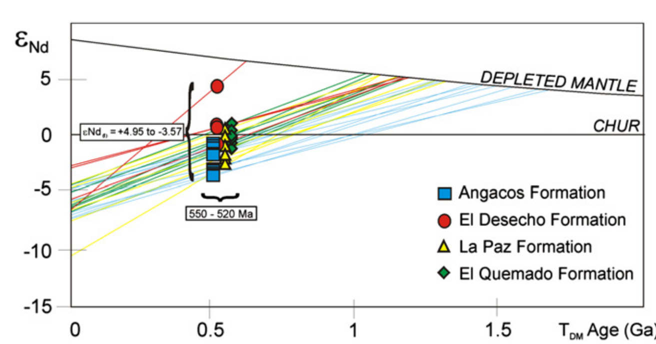

Fig. 7. Plot of εNd against age of El Quemado, La Paz, El Desecho, and Angacos formations (Caucete Group). See the εNd evolution at their depositional age (approximately 550–520 Ma) with a range between approximately +5 to −4.

a contribution from UCC, mainly composed of felsic rocks. Also, some samples showed very high Zr/Sc ratio indicating a high extent of recycling of sediments, the major value is from Angacos Formation (Zr/Sc = 249). Notwithstanding, in few samples can be recognized the presence of mafic rocks in their source area (VVL68 El Quemado Formation, PP503 La Paz Formation, and M11 El Desecho Formation), because the low Th/Sc ratio and concentrations of ferromagnesian elements (Sc, Cr, V, and Co) higher than the average UCC. Particularly sample VVL68 which do not show a negative Eu-anomaly, suggesting influence of juvenile sources (mantle derived), e.g.: island-arc basalts and andesites. The $\varepsilon Nd_{(t)}$ above −5 (between +4.95 and −3.57), support the supply of a juvenile source (mantle derived) in the area. However, provenance contribution from upper continental crust is also demonstrated, especially in the Angacos Formation ($\varepsilon Nd_{(t)}$ ca. −3.57).

In summary, we consider that the sediments source area in the Caucete Group is composed by rocks of different compositions. There is a clear provenance of felsic rocks from UCC along with mafic rocks (mantle derived). A provenance mixed model could involve a Paleoproterozoic source (old felsic rocks) with a Mesoproterozoic–Neoproterozoic (juvenile) source. This model is in accordance with the geochemical provenance indicators and also with the geochronological data from detrital zircon ages that suggest Paleoproterozoic, Mesoproterozoic and Neoproterozoic sources.

5.1. Tectonic setting

The tectonic setting indicated by geochemical data for the El Quemado, La Paz, and El Desecho formations is coherent with the tectonic setting suggested by Naipauer et al. (2010) as a rifted margin. This interpretation is based on the tectonic discrimination diagram (Sc–Th–Zr/10), sedimentary protolith and the igneous zircon source ages (550–530 Ma) that should had been close in age to the time of deposition of the Caucete Group (Naipauer et al., 2010). This igneous source (probably juvenile) is consistent with positive $\varepsilon Nd_{(t)}$ data found in the units mentioned. On the other hand, the evolution to a carbonate-dominated passive margin in the Angacos Formation is supported by the higher Zr/Sc ratio and the increase in the sediments recycling.

6. Regional implications

Determining crustal affinities of deformed and metamorphosed sedimentary rocks and their potential source areas can be quite complex (Bream et al., 2004). The age, correlations with the surrounding units, and the origin of the terrane where they originated should be considered. These are the biggest problems when comparing the metasediments data with their potential source areas. Despite these difficulties, we will discuss and compare the geochemical data obtained for the Caucete Group discussed previously with the Grenville basement of Cuyania, and with neighboring rocks of similar age of south western Gondwanan provenance. Finally, we compare the data with sources close to Ouachita embayment in the southern margin of Laurentia.

6.1. Cuyania basement

The Cuyania basement is comprised mainly of Mesoproterozoic rocks from Sierra de Pie de Palo, Sierra de Umango, Precordillera xenoliths, and San Rafael and Las Matras blocks (Fig. 1a; see review by Ramos, 2004). The origin of Cuyania basement from Laurentia has been supported by the presence of Grenville-age basement in the Precordillera and Pie de Palo areas with Pb isotopic signature and sedimentary covers similar to that from the southern Laurentia Grenville province (Astini et al., 1995; Kay et al., 1996; Casquet et al., 2001; Vujovich et al., 2004).

The Sierra de Pie de Palo crystalline basement includes a suite of schists, marbles, migmatites, leucogranites, and mafic to ultramafic metaigneous rocks, grouped in the Pie de Palo Complex (Ramos et al., 1998; Ramos and Vujovich, 2000). The detrital zircons of Mesoproterozoic age of the Caucete Group may have been supplied from Pie de Palo (Cuyania) basement (Naipauer et al., 2010). The geochemistry and Nd isotope composition of orthogneisses and mafic rocks from Pie de Palo Complex, and the Neoproterozoic Quebrada Derecha orthogneiss (see Fig. 1b), showed a clear juvenile Mesoproterozoic composition ($\varepsilon Nd_{(t)}$ between +8.0 and −0.2) and T_{DM} model ages recalculated with DePaolo (1981) between 1.65 and 0.94 Ga (Baldo et al., 2006; Rapela et al., 2010). Moreover, most of the Mesoproterozoic basement of Cuyania contain a significant juvenile component (Rapela et al., 2010; and references therein).

This data suggest that the Mesoproterozoic and Neoproterozoic basement rocks of the Cuyania basement could probably constitute the juvenile sources with T_{DM} ages between 1.70 and 1.00 Ga observed in the Caucete Group. Also, the contribution from mafic rocks (juvenile material) based on the trace elements and REE analysis presented would allow to suggest the supply from the mafic and ultramafic Pie de Palo Complex.

The provenance of crustal sources is more difficult to explain from the Cuyania basement. Although the Pie de Palo Complex includes paragneisses and schists (meta-greywackes) similar to the UCC (Vujovich and Kay, 1998; Vujovich, 2003) that could have been the older felsic component that was observed in most of the analyzed samples of Caucete Group (Vujovich, 2003).

6.2. Comparison with metasedimentary rocks from southern Gondwana margin

There are significant differences between the detrital zircon ages patterns of the Caucete Group and those of Neoproterozoic-Cambrian sedimentary rocks from the western Gondwana margin of the Central Andes. Gondwanan metasedimentary units, are characterized by bimodal and multimodal distributions of detrital zircon ages, with Pampean (ca. 520 Ma), Brazilian (ca. 635 Ma) and Grenville-Sunsás (ca. 900–1200 Ma) peaks (Schwartz and Gromet, 2004; Escayola et al., 2007; Chew et al., 2008; Adams et al., 2008; Collo et al., 2009; Drobe et al., 2009; and references therein). To the present knowledge there is a gap in detrital zircon ages between ca. 1450–1300 Ma in western Gondwana samples while these ages are the main components of the detrital zircons in the Caucete Group (see discussion in Naipauer et al., 2010).

The data obtained for several areas considered to had been part of the south western margin of Gondwana as Sierra de San Luis (see Fig. 1a) (Nogolí, Pringles, and Conlara Metamorphic Complexes, and San Luis Formation) and Cordillera Oriental (Puncoviscana Formation) comprise $\varepsilon Nd_{(t)}$ values (where $t = 540$ Ma) between −3.0 and −7.8, and T_{DM} ages (recalculated with DePaolo, 1981) between 1.64 and 1.36 Ga (20 samples; Drobe et al., 2009). In the metasedimentary rocks of the Sierra de Famatina (Negro Peinado and Achavil formations; Collo et al., 2009), the $\varepsilon Nd_{(t)}$ ($t = 500$ Ma, the maximum depositional age) for both units fall between −7.39 and −9.83, and the T_{DM} ages (DePaolo, 1981) between 1.81 and 1.58 Ga (12 samples).

In the Caucete Group $\varepsilon Nd_{(t)}$ is highly positive compared to those from Sierra de San Luis, Cordillera Oriental and Sierra de Famatina, indicating a major participation of mafic juvenile compositions. The T_{DM} ages overlap with values between 1.70 and 1.30 Ga, but there are T_{DM} ages younger (0.63, 1.10 and 1.20 Ga) that are not represented in the units mentioned of the south western margin of Gondwana. Consequently, we suggest that the Nd isotope

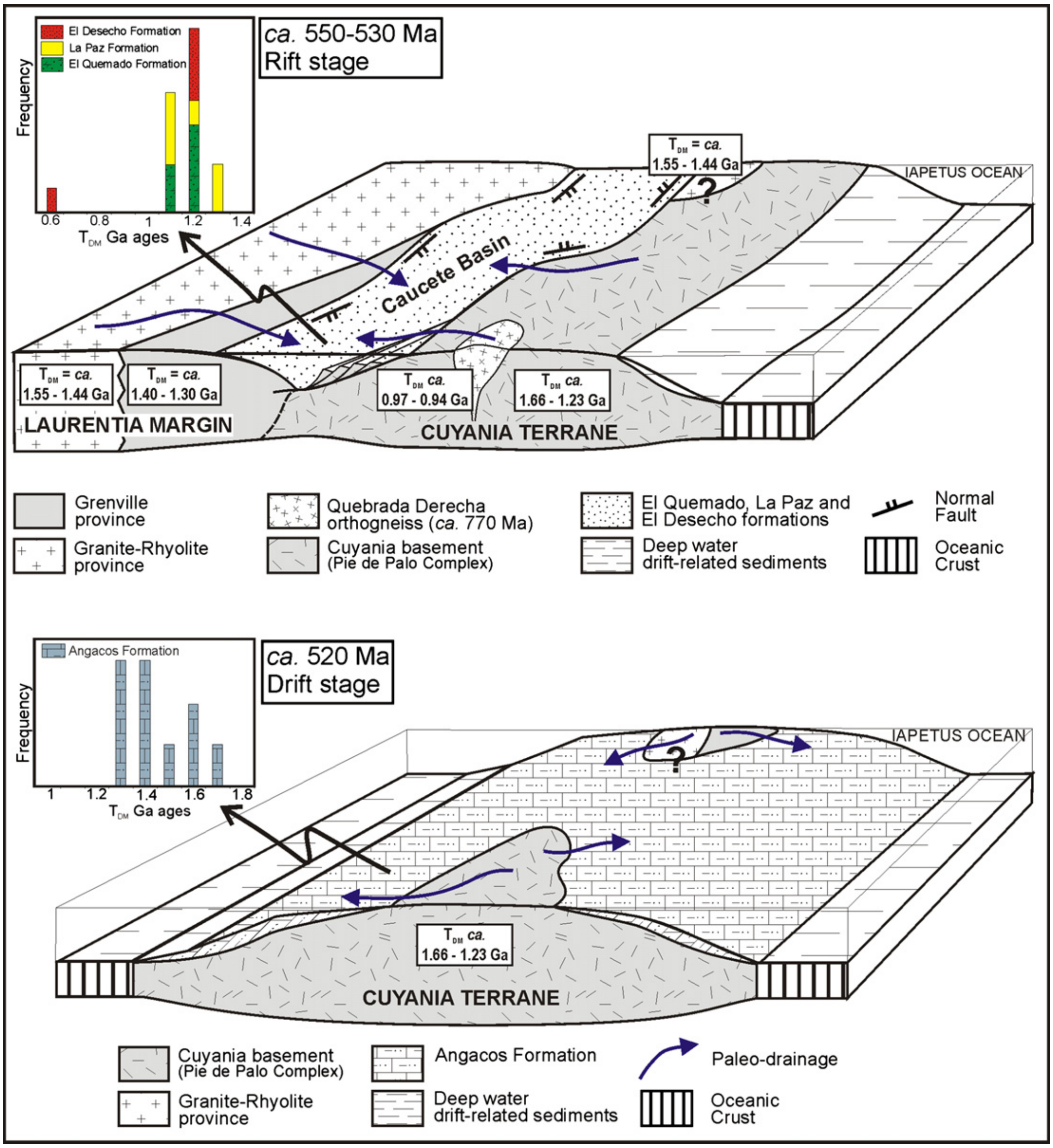

Fig. 8. Source regions and tectonic evolution of the Cuyania terrane for rift (ca. 550–535 Ma) and drift (ca. 520–510 Ma) stages, according with inferred time of deposition of the Caucete Group. See the T_{DM} frequency plots of the Fig. 6 for help. The T_{DM} ages of the source regions of the Laurentia margin are from Barnes et al. (2002; and reference therein) and of the Cuyania basement from Baldo et al. (2006) and Rapela et al. (2010; and reference therein).

signatures of the Caucete Group are different with respect to those of the units from the south western Gondwana margin.

The discrepancies in patterns of detrital zircon ages and geochemical (principally Sm–Nd) data between the Caucete Group metasedimentary rocks and the neighboring units autochthonous to the southern margin of Gondwana, allow to consider that Gondwanan terranes was not a provenance source for the Caucete Group.

6.3. Laurentia provenance

Since the Mesoproterozoic basement of Cuyania is comparable to the Grenville basement of the central part of the southern margin of Laurentia (Kay et al., 1996; Vujovich and Kay, 1998; Casquet et al., 2001), this could represent a possible source area for the Caucete Group. The basement of Central and West Texas in North America is characterized by isolated outcrops of Mesoproterozoic metaigneous and metasedimentary rocks (Roback, 1996; Mosher, 1998; Carrigan et al., 2003, and references therein). The most important exposures are in the Llano Uplift, in the Van Horn area, and in the Franklin Mountains. The T_{DM} model ages are characterized by a range of about 1.40–1.30 Ga and εNd are positive, indicating a juvenile source (Barnes et al., 2002). Also, in West Texas there are outcrops of the Granite-Rhyolite magmatic province, which is mainly a granitic and rhyolite sequence with U–Pb ages ca. 1360 Ma and Sm–Nd model ages that range from 1.56 to 1.44 Ga (Barnes et al., 2002). The Sm–Nd isotopic character of the southern Laurentian basement is clearly comparable to that of the Caucete Group. This sector could have formed part of the source area, prior to separation of the Cuyania terrane from the Laurentian margin, during the deposition of El Quemado, La Paz, and El Desecho formation; and for the Angacos Formation probably the source region was the Cuyania basement itself (Fig. 8).

7. Conclusions

1) The geochemical analysis and previous geochronological studies on the Caucete Group support the origin of the detrital rocks from

Paleoproterozoic, Mesoproterozoic and Neoproterozoic sources. Furthermore, we differentiated the composition of the source areas, integrated for felsic rocks (UCC) as so likewise by mafic rocks (mantle derived). A provenance mixed model was interpreted, with a Paleoproterozoic source (old felsic rocks) related with a Mesoproterozoic–Neoproterozoic (juvenile) source. We emphasize that the provenance mixed model is in agreement with a rifted margin (El Quemado, La Paz, and El Desecho formations) that evolved into a passive margin carbonate platform (Angacos Formation) as the tectonic setting of deposition, these data are supported by the highest value of Zr/Sc and an increase in the recycling of the sediments.

2) Mesoproterozoic and Neoproterozoic rocks of the Cuyania basement were interpreted as responsible for the juvenile component defined in the Caucete Group. Also, the derivation from mafic and ultramafic rocks belt from Pie de Palo Complex was evidenced through the trace elements and REE analysis. The contribution from typical UCC sources was more difficult to explain from Cuyania basement. However, the paragneisses and schists (meta-greywackes) of the Pie de Palo Complex probably could have been the felsic component that was observed in the Caucete Group.
3) We do not consider Gondwana as a provenance source based on the discrepancies in the geochemical (mainly Sm–Nd) results and the patterns of detrital zircon ages between the Caucete Group metasedimentary rocks and the neighboring units autochthonous to the south western margin of Gondwana.
4) Finally, the Sm–Nd isotopic signature of the Caucete Group is comparable with those from the southern Laurentian basement, suggesting that this sector could have formed part of the source area. Hence the geochemical results are in accordance with an allochthonous origin, derived from southern Laurentia, for the Caucete Group (Cuyania terrane).

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