Zircon and whole-rock Nd-Pb isotopic provenance of Middle and Upper Ordovician siliciclastic rocks, Argentine Precordillera

JAMES D. GLEASON*, STANLEY C. FINNEY[†], SILVIO H. PERALTA[‡], GEORGE E. GEHRELS[§] and KATHLEEN M. MARSAGLIA[¶]

*Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109, USA (E-mail: jdgleaso@umich.edu)

†Department of Geological Sciences, California State University at Long Beach, Long Beach, CA 90840, USA

‡CONICET, Universidad Nacional de San Juan, 5400 Rivadavia, San Juan, Argentina §Department of Geosciences, University of Arizona, Tucson, AZ 85721, USA ¶Department of Geological Sciences, California State University at Northridge, Northridge, CA 91330, USA

ABSTRACT

Graptolite-bearing Middle and Upper Ordovician siliciclastic facies of the Argentine Precordillera fold-thrust belt record the disintegration of a longlived Cambro-Mid Ordovician carbonate platform into a series of tectonically partitioned basins. A combination of stratigraphic, petrographic, U-Pb detrital zircon, and Nd-Pb whole-rock isotopic data provide evidence for a variety of clastic sediment sources. Four Upper Ordovician guartzo-lithic sandstones collected in the eastern and central Precordillera yield complex U-Pb zircon age spectra dominated by 1.05–1.10 Ga zircons, secondary populations of 1.22, 1.30, and 1.46 Ga, rare 2.2 and 1.8 Ga zircons, and a minor population (<2%) of concordant zircons in the 600–700 Ma range. Archaean-age grains comprise <1% of all zircons analysed from these rocks. In contrast, a feldspathic arenite from the Middle Ordovician Estancia San Isidro Formation of the central Precordillera has two well-defined peaks at 1.41 and 1.43 Ga, with no grains in the 600–1200 Ma range and none older than 1.70 Ga. The zircon age spectrum in this unit is similar to that of a Middle Cambrian quartz arenite from the La Laja Formation, suggesting that local basement rocks were a regional source of ca 1.4 Ga detrital zircons in the Precordillera Terrane from the Cambrian onwards. The lack of grains younger than 600 Ma in Upper Ordovician units reinforces petrographic data indicating that Ordovician volcanic arc sources did not supply significant material directly to these sedimentary basins. Nd isotopic data (n = 32) for Middle and Upper Ordovician graptolitic shales from six localities define a poorly mixed signal [$\epsilon_{Nd}(450 \text{ Ma}) = -9.6 \text{ to } -4.5$] that becomes more regionally homogenized in Upper Ordovician rocks (-6.2 ± 1.0 ; $T_{\rm DM} = 1.51 \pm 0.15$ Ga; n = 17), a trend reinforced by the U-Pb detrital zircon data. It is concluded that proximal, recycled orogenic sources dominated the siliciclastic sediment supply for these basins, consistent with rapid unroofing of the Precordillera Terrane platform succession and basement starting in Mid Ordovician time. Common Pb data for Middle and Upper Ordovician shales from the western and eastern Precordillera (n = 15) provide evidence for a minor (<30%) component that was likely derived from a high- μ (U/Pb) terrane.

Keywords Ordovician, Precordillera, graptolites, provenance, isotopes, zircon.

INTRODUCTION

The Argentine Precordillera (Fig. 1) has long been recognized as an early Palaeozoic suspect terrane of probable Laurentian origin, based on a combination of paleomagnetic, faunal, stratigraphic, geochronologic, isotopic and structural evidence (e.g. Borello, 1971; Bond et al., 1984; Ramos et al., 1986; Ramos, 1988; Dalla Salda et al., 1992a,b; Dalziel et al., 1994, 1996; Astini et al., 1995; Benedetto et al., 1995; Dalziel & Dalla Salda, 1996; Kay et al., 1996; Thomas & Astini, 1996; Dalziel, 1997; Astini, 1998a; Benedetto, 1998; Keller et al., 1998; Rapalini & Astini, 1998; Astini & Thomas, 1999; Keller, 1999; Thomas et al., 2001, 2004). The Cambrian-Middle Ordovician carbonate platform that is the most distinctive feature of the Precordillera Terrane contains the endemic Early Cambrian olenellid trilobite fauna at its base, whose only known counterparts exist in Laurentia (Borello, 1971; Ross, 1975). Other fossils of apparently strictly Laurentian affinity (e.g. Early Cambrian Salterella) have also been identified in the Precordillera

carbonate platform (Astini et al., 2004), reinforcing a large body of evidence arguing for close connections to the North American Appalachian-Ouachita margin at this time (Bond et al., 1984; Astini et al., 1995). Here, new geochemical data are presented, from Middle and Upper Ordovician rocks that bear on the origin, evolution and tectonic setting of siliciclastic sedimentary basins which formed atop the collapsing Cambrian-Mid Ordovician carbonate platform of the Precordillera Terrane. Disintegration of the *ca* 600 km long carbonate platform resulted in a series of extensional-type basins that received a large influx of clastic sediments starting in Mid Ordovician time (e.g. Astini et al., 1995; Astini, 1998a; Keller, 1999; Astini, 2003). The influx of fine-grained clastics into rapidly deepening marine basins over a wide region of the Precordillera was accompanied locally by episodic pulses of coarse clastic sedimentation including olistostromes, debris flows, conglomerate and turbidites bounded by major unconformities and hiatuses (Astini et al., 1995; Keller et al., 1998; Keller, 1999; Astini, 1998a, 2003; Heredia & Beresi, 2004), a



Fig. 1. Location map of Ordovician sections sampled within the Precordillera fold-thrust belt of northwestern Argentina (limestone pattern). The Frontal Cordillera of the high Andes of Argentina (Chilenia Terrane) is to the west. The Precordillera Terrane incorporates the Precordillera fold-thrust belt, plus areas to the south and to the east including the westernmost Sierras Pampeanas (e.g. Sierra de Pie de Palo). East of this, rocks of the Sierra de Famatina represent an Ordovician volcanic arc constructed on basement of the Pampean Terrane, defined by rocks of the eastern Sierras Pampeanas recording a 520 Ma high grade metamorphic event. 1 – Villicum sub-basin, Don Braulio Creek; 2 – Guandacol sub-basin, Quebrada de las Plantas/Río de los Piojos; 3 – San Juan sub-basin, Cerro La Chilca; 4 – San Isidro sub-basin, San Isidro Creek; 5 – Río San Juan (Calingasta section), western Precordillera; 6 – Río Jáchal (Los Túneles section), western Precordillera.

pattern that continued into the Silurian and Devonian (Von Gosen, 1995; Keller, 1999).

The tectonic setting of these basins (Fig. 2) has been controversial (e.g. Astini et al., 1995; Von Gosen, 1995; Astini, 1998a; Keller, 1999). Many workers agree that a proximal, seismically active continental shelf probably acted as a primary sediment source at times (e.g. Keller, 1999), although mature volcanic arc sources may have also been important (e.g. Astini et al., 1995). Keller (1999) concluded that a block-fault, halfgraben style of tectonic subsidence best accounted for the Middle Ordovician through Devonian succession of the Precordillera (Fig. 2A). Sea-level fluctuations probably do not account for the full scale and diachronous nature of hiatuses and paraconformities (submarine erosional surfaces) within the Ordovician siliciclastic succession (Fig. 3), which is better explained by localized tectonic effects on the sedimentary system (Keller, 1999; Astini, 2003). For this paper, Nd-Pb wholerock isotopic data were obtained, U-Pb detrital zircon ages, and sandstone petrographic data from samples dated by graptolite biostratigraphy in an effort to address the following questions:

1 Did a Mid Ordovician rifting event (Fig. 2A) mark the disintegration of the Precordillera platform and final separation of the Precordillera platform from a Laurentian marginal plateau (Keller *et al.*, 1998; Rapela *et al.*, 1998a; Keller, 1999)? or,

2 Did subduction and accretion of the Precordillera Terrane (Fig. 2B) against the Ordovician Famatina Arc (Astini *et al.*, 1995; Thomas & Astini, 1996; Astini, 1998a; Astini & Thomas, 1999; Casquet *et al.*, 2001; Thomas *et al.*, 2002; Thomas & Astini, 2003) produce a peripheral foreland basin that began undergoing flexural extension in the late Mid Ordovician (Astini, 1998a, 2003)? or,

3 Did migration of the Precordillera Terrane along the proto-Andean margin of Gondwana (Fig. 2C) occur via right-lateral strike-slip faults (Baldis *et al.*, 1989; Aceñolaza & Toselli, 2000; Aceñolaza *et al.*, 2002; Finney *et al.*, 2003), producing extensional pull-apart basins atop the Precordillera platform (Finney, 2006)?

Earlier suggestions that collision between Laurentia and Gondwana in the Mid Ordovician could have produced a continuous Taconic-Famatina arc (Dalla Salda *et al.*, 1992a,b) have largely been discarded based on palaeomagnetic and faunal evidence for a wider Iapetus Ocean at this time (MacNiocaill *et al.*, 1997); however, the idea of an early Palaeozoic extended Texas (Laurentian)



Fig. 2. Cartoons depicting various tectonic settings proposed for Ordovician siliclastic basins of the Precordillera Terrane (PCT). The rift model (A) proposed by Keller (1999) favours detachment of PCT from Laurentia starting in the Mid Ordovician, accompanied by block faulting and half-graben formation. The subduction model (B) proposed by Thomas & Astini (1996) favours foreland extension on the down-going plate, as the PCT approached the Famatina Arc in the Mid Ordovician. The transform model (C) proposed by Aceñolaza *et al.* (2002) and Finney *et al.* (2005) favours pull-apart basin formation starting in the Mid Ordovician as the PCT migrated along the Proto-Andean margin of Gondwana (P.A.M.G.).

Plateau (Dalziel, 1997) between Laurentia and Gondwana still persists. Whether or not the Ordovician siliciclastic basins formed during



Fig. 3. Correlation chart for Ordovician sections sampled in the Argentine Precordillera. Astini (1998a, fig. 3, p. 16), Astini & Thomas (1999, fig. 3, p. 5), Benedetto *et al.* (1999, fig. 2, p. 23), Keller *et al.* (1998), Keller (1999), Albanesi & Ortega (2002, p. 145, fig. 1), Peralta & Finney (2003, fig. 3, p. 51) and Heredia & Beresi (2004, fig. 6) serve as the primary references for correlation of Middle to Upper Ordovician stratigraphic units in the Precordillera (Webby, 1998; Finney, 2005). H, Hiatus; SB, Structural Break. Ordovician basins of the western Precordillera are represented to the right on this diagram (Calingasta and Los Túneles sections). Numbers at top correspond to locations on Fig. 1. Asterisks indicate relative position in sections where sandstones were sampled for detrital zircon (see also Fig. 8).

continental rifting (Keller *et al.*, 1998; Rapela *et al.*, 1998a; Keller, 1999) is predicated partly on the assumption that coeval eugeoclinal rocks (mafic/ultramafic assemblages and abyssal sediments) in the western part of the Precordillera fold-thrust belt are related to eastern Precordillera depositional systems, a concept that has been challenged in the past.

The foreland basin model advocated by Astini et al. (1995), Thomas & Astini (1996), Astini (1998a) and Astini & Thomas (1999) favours basin evolution by lithospheric flexure driven by thrust loading, subduction and accretion along the Famatina Arc (Thomas et al., 2002; Astini, 2003; Thomas & Astini, 2003). Ordovician siliciclastic basin evolution in the Precordillera, which is characterized by rapid, diachronous changes in sedimentation style and regionally developed unconformities, is thus explained by migration of a peripheral forebulge on the downgoing plate (Thomas et al., 2002; Astini, 2003). Certain tectonic elements, such as the inferred forearc basin and subduction complex/accretionary prism (Astini, 2003; López & Gregori, 2004; Ramos, 2004), have yet to be clearly identified across the proposed suture zone dividing the Famatina Arc and the Precordillera Terrane, although evidence has been cited for Ordovician compressional deformation within the Precordillera fold-thrust belt (Astini, 2003).

As an alternative, Aceñolaza *et al.* (2002) considered that Ordovician-Devonian siliciclastic basins of the Precordillera were formed during large-scale right-lateral transport of the Precordillera Terrane along a series of transcurrent faults originating from a hypothetical low-latitude Cambro-Ordovician Gondwanan platform (e.g. Rapela *et al.*, 2003). According to this model, juxtaposition of the Precordillera Terrane against the Famatina Arc did not occur until sometime in the Devonian. Major transcurrent faults of this age are not yet well documented along this segment

of the proto-Andean margin of West Gondwana (Astini & Rapalini, 2003), although ductile shear indicators of Cambrian-Devonian age are well known in basement rocks of the neighbouring Sierras Pampeanas (Von Gosen *et al.*, 1995; Höckenreiner *et al.*, 2003; Simpson *et al.*, 2003). It is worth noting that Keller (1999), in his Ordovician rifting model for the Precordillera Terrane, also envisioned post-Ordovician (Siluro-Devonian) docking between the Precordillera Terrane and West Gondwana, following the Ordovician departure of the Precordillera Terrane from North America (Rapela *et al.*, 1998a).

Despite an array of competing geodynamic models, Astini et al. (1995) and Thomas & Astini (1996) have provided a compelling, widely accepted geodynamic model for an origin of the Precordillera Terrane in the Ouachita Embayment of North America (originally suggested by Dalla Salda et al., 1992a,b), consisting of the following stages: (1) Early Cambrian rifting, (2) Mid Cambrian through Early Ordovician drifting of the Precordillera Terrane as a microcontinent across the Iapetus Ocean, (3) Mid Ordovician docking of the Precordillera Terrane along the Famatina Arc in western Gondwana (Astini et al., 1995; Thomas & Astini, 1996, 2003; Thomas et al., 2002). The presence of voluminous Early to Mid Ordovician bentonites (ca 470 Ma) in the central and eastern Precordillera (Huff et al., 1997; Bergström et al., 1998), which overlap in age with Famatina Arc magmatism (ca 470-500 Ma; Huff et al., 1998; Pankhurst et al., 2000; Fanning et al., 2004), lends strength to the Thomas-Astini model. Finney (2006), on the other hand, has argued, based on graptolite biogeography, that the Famatina Arc occupied a higher latitude position through most of the Ordovician than the Precordillera Terrane, in potential conflict with the Thomas-Astini model. The poor correlation between Ordovician K-bentonites of the Precordillera Terrane carbonate platform and those of Laurentia/Baltica (Samson, 1996; Huff et al., 1998; Thomas et al., 2002) continues to be a strong argument against the Keller (1999) rifting hypothesis.

While close Cambrian connections between Laurentia and the Precordillera Terrane seem well-constrained by various datasets (though see counter-arguments presented by Finney, 2006), the palaeogeography of the Precordillera Terrane during the Ordovician remains less certain. Unambiguous Ordovician palaeomagnetic poles are lacking (Rapalini & Cingolani, 2004), Ordovician fauna exhibit mixed characteristics of Gondwanan and Laurentian paleoplates (Finney, 2006), and strong latitudinal constraints appear only with the latest Ordovician Hirnantian glaciation, well-documented in the Argentine Precordillera and elsewhere in Gondwana (Peralta & Carter, 1990; Buggisch & Astini, 1993; Astini, 2003).

In this paper, new geochemical data are presented that bear on the origin, evolution and tectonic setting of the clastic sedimentary assemblage that accompanied disintegration of the Cambrian-Mid Ordovician Precordillera Terrane carbonate platform starting in Mid Ordovician time. Nd-Pb whole-rock isotopic data, U-Pb detrital zircon ages and sandstone petrography of Middle and Upper Ordovician siliciclastic units from several well-characterized stratigraphic sections in the Precordillera Terrane are used to interpret their provenance. All samples are dated using graptolite biostratigraphy (Finney, 2005), allowing precise regional correlations.

GEOLOGICAL SETTING, SAMPLING AND STRATIGRAPHY

The Argentine Precordillera (Fig. 1) is a physiographic province within the deformed Andean foreland of north-western Argentina (Baldis et al., 1982, 1984; Ramos et al., 1986, 2002). Here, between latitudes ca 29 °S and ca 33 °S, Palaeozoic rocks are exposed in a thin-skinned fold-thrust belt that was generated by shallow, east-dipping (flat-slab) subduction of the Nazca plate (Jordan et al., 1983; Allmendinger et al., 1990). To the east of the Precordillera are the Laramide-style basement uplifts of the Sierras Pampeanas (Fig. 1). The Sierra de Famatina (Fig. 1), and neighbouring ranges in the western Sierras Pampeanas, expose part of an Ordovician volcanoplutonic arc complex that occupies an area between the West Gondwanan craton and the Precordillera Terrane (Pankhurst et al., 1998). Siliciclastic and volcaniclastic rocks, along with coeval volcanic and plutonic rocks, collectively constitute a Famatinian Lower and Middle Ordovician back-arc sedimentary assemblage that has been proposed as one possible source for Precordillera Middle and Upper Ordovician siliciclastic rocks (Astini, 2003). Outboard of the Famatina Arc, in the westernmost Sierras Pampeanas, is Mesoproterozoic (ca 1.1 Ga) basement exposed within the Sierra de Pie de Palo (Fig. 1). This basement has been interpreted (Vujovich & Kay, 1998) as being an extension of the Precordillera

Terrane basement (xenoliths of the same age in Miocene volcanics within the Precordillera foldthrust belt indicate the presence of similar basement at depth - Abbruzzi et al., 1993; Kay et al., 1996; although see Galindo et al., 2004 for a different interpretation). Structural relations between this Mesoproterozoic basement and the Early Palaeozoic (Cambrian-Devonian) sedimentary succession of the Precordillera remain uncertain, but it has become widely accepted that *ca* 1.0-1.2 Ga basement is representative of the Precordillera terrane (Kay et al., 1996; Ramos et al., 1998; Sato et al., 2004; Vujovich et al., 2004). The Sierra de Pie de Palo basement complex has also been proposed as one potential source of the Ordovician-Devonian siliciclastic succession of the Precordillera (Loske, 1995; Astini, 2003).

The Precordillera Terrane was originally defined by the extent of its Cambrian-Mid Ordovician carbonate platform, which is considered stratigraphically and faunally unique to South America (Ramos et al., 1998; although see Sprechmann et al., 2004), and by the Grenvillian-age (1.0-1.2 Ga) basement inferred to underlie the Palaeozoic succession (Kav et al., 1996). The dimensions of the original Precordillera Terrane carbonate platform are debatable, but have been estimated to be on the order of 800 km in length or more, with its probable extension into the San Raphael region (34.5 °S) and possibly as far south as 37.5 °S (Astini, 2003; Ramos, 2004). The platform may have been up to 400 km in width, but with the succession thinning substantially to the south from a maximum estimated thickness of ca 2000 m in the north (Keller, 1999; Astini, 1998a). Ramos et al. (1998) introduced the concept of a greater Cuyania terrane that incorporates the Precordillera Palaeozoic succession and its probable southern extension into the San Raphael region, along with adjacent parts of the western Sierras Pampeanas (e.g. Sierra de Pie de Palo) that contain Grenvillian-age basement (Kay et al., 1996; Ramos et al., 1998; Ramos, 2004). Though the exact fault boundaries of the Cuyania/Precordillera Terrane are not well defined, the limits at present are inferred by many workers to be a palaeo-convergent boundary (or suture zone) to the east along the Ordovician Famatina Arc (Valle Fértil lineament – Ramos et al., 1986, 1998, 2002; Astini et al., 1995; Thomas & Astini, 1996, 2003; Astini & Thomas, 1999; Casquet et al., 2001; Thomas et al., 2002; Ramos, 2004), and a Silurian/Devonian convergent margin to the west that separates the western basins of the Precordillera fold-thrust belt from the Siluro-Devonian Chilenia

arc terrane of the Frontal Cordillera (Ramos et al., 1986; Astini et al., 1995; Thomas & Astini, 1996; Davis et al., 2000; Gerbi et al., 2002). The latter boundary, and inferred boundaries to the north and south, are obscured by multiple episodes of tectonic deformation culminating in recent Andean convergent margin tectonics (e.g. Lucassen et al., 2000; Gerbi et al., 2002; López & Gregori, 2004; Ramos, 2004). The boundary to the west is inferred to coincide approximately with the westernmost outcrops of deep-water Ordovician facies found along the Calingasta-Rodeo-Uspallata valley (Astini, 2003; Ramos, 2004). On the other (eastern) side, major Palaeozoic basement shear zones have been mapped in parts of the western Sierras Pampeanas (Höckenreiner et al., 2003; Simpson et al., 2003), including the Sierra de Pie de Palo (Ramos et al., 1998; Vujovich et al., 2004), suggesting a complex and protracted history of basement deformation along the eastern margins of the greater Precordillera (Cuyania) Terrane.

In a more regional geological context, the Precordillera Terrane is here considered distinct from Brasiliano/Trans-Amazonian crustal domains (equivalent to 900-500 Ma Pan-African, and 2.2-2.0 Ga Eburnian mobile belts, respectively) that characterize parts of the West Gondwanan craton, including areas of the eastern Sierras Pampeanas that were affected by a *ca* 520 Ma (Pampean) high-grade metamorphic event as yet unrecorded in Precordillera Terrane basement (Ramos, 1988, 2004; Rapela et al., 1998b). An overlap sedimentary assemblage of Carboniferous age, underlain by a regional angular unconformity, requires that the Precordillera Terrane and adjacent parts of West Gondwanaland (including the Famatina Arc) had acquired their present positions relative to each other by that time (Baldis & Chebli, 1969; Baldis et al., 1982; Ramos et al., 1984; Azcuy & Carrizo, 1995; Carrizo & Azcuy, 1997).

As described above, although the exotic nature of the Precordillera Terrane to this part of West Gondwanaland is widely recognized, different scenarios for the tectono-palaeogeographic history of the Precordillera Terrane have persisted. Similarities in (1) basement ages and basement Pb isotopes (Kay *et al.*, 1996) between the Precordillera and the southern margin of Laurentia, (2) the Early Cambrian low palaeolatitude of both the Precordillera and the Ouachita Embayment (Rapalini & Astini, 1998), and (3) Cambrian biogeography, including a distinctively Laurentian fauna (90% or more of all trilobite genera according to Vaccari, 1995) of the Cambrian Precordillera Terrane, becoming progressively more Gondwanan in character upsection starting in the Mid Ordovician (Benedetto, 1993, 1998; Astini et al., 1995; Vaccari, 1995), make for a compelling argument favouring the microcontinent model outlined in Thomas & Astini (1996). An origin along the Ouachita rifted margin of North America has therefore largely superseded in the literature the original model of Bond et al. (1984), which favoured an origin along the Appalachian rifted margin based on similarities in stratigraphy and thermal subsidence histories of the Appalachian and Precordillera Terrane carbonate platforms. Thomas & Astini (1999) offer an explanation for the disparate subsidence histories of the Ouachita rifted margin and the Precordillera Terrane platform as a simple-shear conjugate rift pair, documenting a close coincidence in timing of riftrelated events between the two, and new detrital zircon evidence for shared clastic sediment sources in Early Cambrian rift assemblages between the two regions (Thomas et al., 2004). Finney et al. (2005) and Finney (2006) have recently called some of these interpretations into question, citing detrital zircon ages more indicative of a Gondwanan affinity for the Precordillera Terrane, and faunal patterns that conflict with the prevailing models.

Seventy-nine samples of graptolite-dated shale were collected from Middle and Upper Ordovician sections representing a total of six localities in the eastern and western Precordillera for Nd-Pb isotopic work (Fig. 1). Four Upper Ordovician sandstone samples and one Middle Ordovician sandstone were also collected from three localities in the eastern and central Precordillera for U-Pb detrital zircon geochronology and sandstone petrography. Salient points of the stratigraphy and sampling of these sections is given below, and in Fig. 2.

Villicum sub-basin, Eastern Precordillera

Don Braulio Creek, Villicum Range (San Juan Province)

The siliciclastic succession at Don Braulio Creek (Figs 1 and 3) spans upper Middle Ordovician through Devonian (Volkheimer *et al.*, 1981; Peralta, 1985, 1986, 1990; Peralta & Baldis, 1990; Astini, 1992). Here, the exposed contact between San Juan Formation outer (deep)-ramp thickbedded limestones and overlying Gualcamayo Formation graptolite-rich black shales (*P. tentaculatus* Zone) represents a regionally recognized platform drowning unconformity (Baldis & Beresi, 1981; Astini, 1994; Astini *et al.*, 1995; Keller, 1999). At Don Braulio Creek, the Gualcamayo Formation of late Mid Ordovician age (Sarmiento, 1985; Peralta, 1993b, 1995) is characterized by 60 m of relatively monotonous black shale, exhibiting little change in lithology upsection above a somewhat more variegated lower part (mudstone/ shale 'transfacies' of Baldis & Beresi, 1981).

The transition into the overlying La Cantera Formation (lower Upper Ordovician; N. gracilis Zone) is marked by a marine erosional surface (paraconformity) and a debris/gravity flow unit at the base of the La Cantera Formation. Clastsupported debris flow conglomerates, containing mixed igneous (dominantly mafic plutonic), orthoquartzite and sedimentary (dominantly sandstone, plus re-worked San Juan limestone and Gualcamavo black shale) clasts, grading into siltstone/sandstone turbidite units with interbedded green silty shale, characterize the lower part of the La Cantera Formation. A crudely fining upward progression gives way to dominantly green silty shales and siltstone/sandstone turbidites towards the top of the La Cantera Formation (total thickness 140 m, Peralta, 1993b). The abundance of turbidites, channel conglomerates, and laterally extensive sheet conglomerate units suggested to some workers a line-source submarine fan-delta (slope apron) depositional environment (Keller, 1999). Flute casts in sandstone units indicate dominantly north-to-south and northwest-to-southeast transport, palinspastically corrected (Peralta, 1993a). Primary sources of coarse clastics could have been active fault scarps along uplifted fault blocks, which exposed mainly local lithologies of the platform and basement to erosion adjacent to the deepening Villicum subbasin (Von Gosen, 1995; Keller, 1999). Astini (1998a, 2003) inferred different source areas for rip-up clasts derived from stratigraphically underlying units, vs. clasts of associated igneous and metamorphic rock brought in from sources to the east as part of a regionally developed clastic wedge (Astini, 2003). Interbedded debris flow conglomerates of the La Cantera Formation containing mixed igneous and sedimentary clasts show that locally exposed lithologies of the carbonate platform and re-worked parts of the Ordovician silicilastic succession (Gualcamayo Formation) were combined with rounded cobbles of basement lithologies external to the Villicum sub-basin (Astini, 2003).

The base of the overlying Don Braulio Formation (total thickness 70 m) is marked by a para-

conformity (erosional hiatus) with relief in places of several metres, and a marine glacial diamictite, up to 20 m thick (Peralta & Carter, 1990, 1999) characterized by rounded and faceted pebbles, cobbles and imbricated boulders (many with oriented glacial striations) set in a fine-grained, clavey matrix. This stratigraphic level corresponds to the Hirnantian Gondwanan glaciation, and coincides with a sea-level low-stand (Astini, 2003). Upsection, a thick transgressive sequence of conglomerates, sandstone, siltstone and fossiliferous shale within the Normalograptus persculptus Zone (Benedetto, 1986; Peralta, 1990) coincides with the late Hirnantian sea-leavel rise (Sánchez et al., 1991; Buggisch & Astini, 1993; Peralta & Carter, 1999) and persists into the lower Silurian (Peralta, 1985). A paraconformity separates the Don Braulio Formation from the overlving Rinconada Formation of Siluro-Devonian age, which marks a return to dominantly wildflysch (debris flow/olistostrome) deposits including >100 m olistoliths of San Juan limestone derived from local continental shelf sources.

A remarkable feature of the Ordovician succession at Don Braulio Creek is the lengthy hiatus represented by the paraconformity separating the La Cantera and Don Braulio formations, which is well-constrained by graptolite biostratigraphy (Fig. 3). What is missing is the whole upper part of the Lower Stage of Upper Ordovician, and the entire Middle Stage of the Upper Ordovician. Thus, ca 12 Ma of the ca 17 Ma duration of the Late Ordovician is missing at the paraconformity, which by contrast is an interval marked by deposition in the Rio de los Piojos section at Guandacol, represented by the Las Vacas and Trapiche formations (see below). It is noteworthy that to the south of Don Braulio Creek, olistostrome, debris flow and conglomerate of the La Pola Formation (lower Upper Ordovician; Astini, 2001; C. bicornis Zone) fills part of this gap between the La Cantera and Braulio formations; but nevertheless the hiatus represented by this gap is still significant (Fig. 3). The absence of this unit at Don Braulio Creek suggests impressive relief at the erosional surface at the base of the Hirnantian glacio-marine diamictite. At Don Braulio Creek, two sandstone units from the La Cantera Formation, one near the base, and one near the top, were sampled for sandstone petrography and U-Pb detrital zircon dating. Both are within the graptolite zone of Nemagraptus gracilis. A total of 27 shale samples from the Ordovician succession at Don Braulio Creek (Gualcamayo through Don Braulio formations)

were also collected for Nd-Pb whole-rock isotopic analysis.

Guandacol sub-basin, Northern Precordillera

Quebrada de las Plantas/Rio de los Piojos (Guandacol Province)

The Middle to Upper Ordovician siliciclastic succession in the Guandacol region of the Northern Precordillera (Figs 1 and 3) is similar to that of Don Braulio Creek, with the following important exceptions: (1) the drowning unconformity that marks the transition from dominantly carbonate platform sedimentation to siliciclastic sedimentation occurs two graptolite zones earlier than at Don Braulio Creek (Cuerda & Furque, 1975; Astini et al., 1995; Keller, 1999), with deposition of Gualcamayo Formation black graptolitic shales beginning in the early Mid Ordovician (I. v. maximus Zone) above deep outer ramp limestones of the San Juan Formation (Ortega et al., 1993), and (2) the Ordovician siliciclastic assemblage is thicker in the Northern Precordillera (>1200 m). Thomas & Astini (2003) and Thomas et al. (2002) hypothesized a coarsening-upward synorogenic (Oclovic) clastic wedge derived from eastern sources for the Ordovician siliciclastic succession in this part of the Precordillera.

As at Don Braulio Creek, in the Guandacol subbasin the deposition of Gualcamayo Formation graptolitic shales (P. tentaculatus Zone) is terminated by an erosional unconformity (Fig. 3), followed by a thick succession of olistrostromes, conglomerates, and turbidites (Astini, 1998a, 2003). This assemblage, the Las Vacas Formation (C. bicornis Zone), commences in the lower Upper Ordovician (Ortega et al., 1983; Astini et al., 1995; Astini, 1998a,b, 2003; Cuerda et al., 2004) and contains clast populations similar to the La Cantera Formation of the Villicum subbasin. Though often considered its stratigraphic equivalent, the Las Vacas Formation is one graptolite zone younger than the La Cantera Formation at Don Braulio Creek (Baldis et al., 1982; Peralta, 1986, 1990). The Ordovician siliciclastic succession of the Guandacol sub-basin (including younger Upper Ordovician turbidites of the Trapiche Formation) may have been deposited in a submarine fan/slope-apron environment in evolving grabens/half grabens that received sediment from both proximal (local fault scarp) and distal (hinterland) sources (Astini, 1998a; Keller, 1999). One sandstone from the lower conglomerate unit of the Las Vacas Formation was sampled for sandstone petrography and U-Pb detrital zircon dating. A total of 19 black graptolitic shales (Gualcamayo Formation) and silty shales (Las Vacas Formation) were collected at this section.

San Juan sub-basin, Central Precordillera

Cerro La Chilca (San Juan Province)

At Cerro La Chilca in the eastern part of the central Precordillera (Fig. 1), a thick continuous section (ca 100 m) of outer and middle ramp carbonate platform facies of highly fossiliferous (nautiloids, trilobites, brachiopods, sponges, bryozoans and crinoids, etc.) upper San Juan Formation (upper Lower to lower Middle Ordovician) is exposed (Fig. 3). A prominent hardground is present near the top of the San Juan Formation, marking the early Mid Ordovician sea-level low-stand (Albanesi et al., 1995; Astini et al., 1995; Astini, 1998a). This open platform environment was terminated by deposition of deep distal ramp/slope deposits of the Middle Ordovician Gualcamavo Formation (P. tentaculatus Zone), which here exhibits a transitional character with alternating siliciclastic and thin limestone beds over several metres. It is overlain paraconformably by black and grey silty shales of the Los Azules Formation (lower Upper Ordovician; N. gracilis Zone; Peralta, 1998). The Gualcamayo Formation at Cerro La Chilca is represented by <10 m of interlayered carbonate and calcareous fossiliferous shale that terminates at an unconformity (Cuerda & Furque, 1985; Peralta, 1998; Ortega & Albanesi, 2000). This sequence represents the lower Member of the Gualcamayo Formation as defined by Peralta (1993a) and Astini (1994). This transitional facies is not recognized by Keller (1999) as Gualcamayo Formation, but as a transitional facies of the Los Azules Formation (N. gracilis Zone; Cuerda & Furque, 1985; Cuerda, 1986; Astini & Benedetto, 1992; Ortega, 1995); however, the shale sample analysed from this unit is a time equivalent of samples collected from the lower Gualcamayo Formation of the Villacum and Guandacol subbasins. The Los Azules Formation at Cerro La Chilca correlates with the *N. gracilis* zone, which is lower Upper Ordovician (Fig. 3). The C. bicornis zone does not occur at Cerro La Chilca. As at Don Braulio Creek, there is a paraconformity between the N. gracilis zone and the overlying Hirnantian, which is represented at Cerro La Chilca by debris flow deposits of the Don Braulio Formation (Astini & Benedetto, 1992; Peralta,

1998). Two lower Middle Ordovician carbonate beds of the upper San Juan Formation were sampled to extract the detrital clay fraction for isotopic analysis, and one calcareous shale of the Gualcamayo Formation higher up in the section was also sampled. The graptolite-rich black shales of the Los Azules Formation are well exposed at the base and top of the stratigraphic section at the Cerro La Chilca, where it was sampled at 1 m intervals. A total of 12 graptolitic shale samples were collected from this part of the section.

San Isidro sub-basin, Central Precordillera

San Isidro Creek (Mendoza Province)

The Lower Ordovician San Juan Formation is not exposed at San Isidro Creek (Figs 1 and 3), but olistoliths of Cambrian carbonate platform lithologies are found in olistostrome/debris flow units of Mid Ordovician age (P. distichus Zone) at the base of the exposed section sampled, and in nearby sections. The largest olistolith is the giant San Isidro olistolith of Middle Cambrian age (>1 km in length). These chaotic units, and several meters of overlying green shale with thin sandstone interbeds, have recently been redefined at San Isidro Creek as the Estancia San Isidro Formation (Heredia & Beresi, 2004). An abrupt change marks the unconformable contact with graptolitic black shale, turbidites and conglomerate of the *C. bicornis* Zone (lower Upper Ordovician) of the Empozada Formation. The Lower Member (ca 50 m) of the Empozada Formation is separated by a paraconformity from the coarse sandstone/siltstone deposits of the Upper Member. The Lower Member is composed mainly of graptolite-rich black shale (*C. bicornis* Zone), becoming more silicified upsection. At the top of the *C. bicornis* Zone, there is a conglomerate with large rounded boulders of granite, limestone and sandstone in the black shale matrix (Heredia & Beresi, 2004). The upper ca 20 m of the Lower Member above the conglomerate is composed of silicified shales containing graptolites of the D. complanatus and D. ornatus Zones (separated by a paraconformity from the *C. bicornis* Zone). Sandstones within the Lower Member have palaeocurrent cross-bedding indicators showing both east- and west-directed transport (Gallardo et al., 1988; Gallardo & Heredia, 1995). The Upper Member of the Empozada Formation (upper Upper Ordovician) rests unconformably on the Lower Member, and has several coarseningupward successions in the sandstones, divided

by a middle section interpreted as a slumped breccia bed. The upper part of the Upper Member also includes a slumped breccia bed containing clasts of the San Juan limestone (Gallardo *et al.*, 1988; Gallardo & Heredia, 1995). Another olistostrome unit, up to the base of the Hirnantian, terminates at a hardground surface within the uppermost Empozada Formation (Heredia & Beresi, 2004). The Empozada Formation is unconformably overlain by Devonian clastics.

Depositional environment and tectonic setting for this sequence of rocks are complex, but may have included deposition in continental margin rift basins with shallowing-upward depocenters (see discussions in Keller, 1999; Heredia & Beresi, 2004). Shales were sampled every 10 m starting at the base of the section along the south side of San Isidro Creek (Heredia & Beresi, 2004), and two sandstone units, one from the top of the Estancia San Isidro (correlative with the Darriwilian stage, upper Mid Ordovician, P. distichus Zone), and one from near the base of the Lower Member of the Empozada Formation (correlative with the lower Upper Ordovician, graptolite zone of C. bicornis), were sampled for petrography and U-Pb detrital age dating. A total of 12 shale samples were collected from the Empozada Formation (proposed type section of Keller, 1999, p. 74, for reference; fig. 3 of Heredia & Beresi, 2004) and the top of the Estancia San Isidro at 10 m intervals for isotopic work (section equivalent to expanded middle inset on p. 62, fig. 31, Keller, 1999, and stratigraphic section A in fig. 30, p. 59; fig. 4 of Heredia & Beresi, 2004).

Western Precordillera

Río San Juan section

The western basins of the Precordillera ('western tectofacies' of Astini et al., 1995) preserve Middle and Upper Ordovician continental margin slope and basin siliciclastic facies distinct from the eastern Precordillera basins (Figs 1 and 3), where depositional links with the Cambro-Mid Ordovician carbonate platform are clearly observed (siliciclastic 'eastern tectofacies' of Astini et al., 1995). Ordovician siliciclastics of Darriwilian (upper Mid Ordovician) age are widely distributed along the eastern margin of the western Precordillera, recording olistostrome/gravity flow and mixed conglomerate/megabreccia/turbidite/ shale units with abundant Cambrian and Lower Ordovician olistoliths (Cuerda et al., 1983: Benedetto & Vaccari, 1992; Vaccari & Bordonaro, 1993; Banchig & Bordonaro, 1994; Astini et al., 1995). These have been considered by some (e.g. Keller, 1999) as being equivalent to the wildflysch unit (Estancia San Isidro Formation) at the base of the section sampled at San Isidro Creek of the central Precordillera. Rocks to the west of here are represented by the Portezuelo del Tontal Formation (dominantly turbidites and conglomerates; N. gracilis Zone; Peralta, 1986, 1990; Peralta et al., 2003), while further west and higher up the Río San Juan drainage are fine-grained siliciclastics of the Late Ordovician Alcaparrosa Formation (Hirnantian-age; N. extraordinarous Zone; Brussa et al., 1999). An inferred timeprogression of westward-fining sedimentation, combined with dominantly west-directed paleocurrents (becoming more basin parallel - NE to SW – farther west in the Precordillera), led Astini et al. (1995) to conclude that Mid-to-Late Ordovician sediment sources for the western basins of the Precordillera lay dominantly to the east; thus, the western basins were considered the distal part of an Ordovician clastic wedge having similar sources as the eastern basins (Astini, 2003).

Unlike in the eastern Precordillera, the timing and onset of basin formation in the western Precordillera is difficult to interpret. Emplacement age of large carbonate platform olistoliths, generally thought to have occurred mainly during the late Darriwilian (Benedetto & Vaccari, 1992; Vaccari & Bordonaro, 1993; Banchig & Bordonaro, 1994), may in fact be Devonian, weakening possible connections to a so-called 'Guandacol' (Darriwilian-age) event (Furque, 1972), thought to have initiated tectonic subsidence in both the western and eastern Precordillera (Keller, 1999). Few good localities exist at present for studying well-preserved and autochthonous graptolites in the western Precordillera. Sediments were probably deposited in environments far offshore and away from oceanic upwelling zones along continental margins where graptolites typically flourished (Finney & Berry, 1997). In addition, rocks of the western Precordillera are intensely tectonized with a greenschist-grade metamorphic overprint (mainly Siluro-Devonian in age; González Bonorino & Aguirre, 1970; Cucchi, 1971; Buggisch et al., 1994; Astini et al., 1995; Von Gosen, 1995), making it difficult to search for fossils on bedding planes. By contrast, in the eastern and central Precordillera, metamorphism is absent or not significant (Astini, 2003).

Along the Río San Juan drainage, the Hirnantian-age Alcaparrosa Formation comprises a several kilometers thick succession of tectonized fine-grained black shale and thin-bedded turbidites with interbedded mafic sills, dikes and lava flows with minor cherts and siltstone/sandstone which Astini *et al.* (1995) interpreted as a distal slope/rise/basin submarine fan facies deposited within an actively rifting ocean basin/near-trench environment. Near the mining town of Calingasta (Figs 1 and 3), Alcaparrosa Formation with wellpreserved Hirnantian graptolites of the lower part of the *Normalograptus extraordinarius–Normalograptus ojsuensis* Zone (Brussa *et al.*, 1999), was discovered in a block of black carbonaceous and phyllitized shale. Samples were taken here at 2– 4 m intervals across *ca* 20 m of vertically exposed section.

Río Jáchal section

Black graptolitic shale of Darriwilian to early Late Ordovician age is exposed in roadcuts above the Jachal River (Figs 1 and 3) as tectonized mudstone/turbidite units several kilometres thick containing interbedded limestone lenses and tectonically interleaved basaltic greenstone. Three samples were collected: two at the wellknown *Los Túneles* roadcut graptolite locality, where late Mid Ordovician-age graptolites (*P. tentaculatus* zone; Ortega *et al.*, 1991) are preserved (assigned to the Yerba Loca Formation – Astini *et al.*, 1995); and another (also assigned to the Yerba Loca Formation) collected from a roadcut outcrop containing *N. gracilis* Zone graptolites (Blasco & Ramos, 1976).

RESULTS AND DISCUSSION

Petrographic analysis and provenance of sandstones

Sandstones were sampled at three different Ordovician sections in the eastern and central Precordillera for petrographic and U-Pb detrital zircon provenance analysis. Four Upper Ordovician sandstones: Las Vacas Formation (n = 1), La Cantera Formation (n = 2), and Empozada Formation (n = 1), represent the Guandacol, Villicum and San Isidro sub-basins, respectively (Figs 1 and 3). A Middle Ordovician sandstone was also sampled from the Estancia San Isidro Formation (n = 1) in the San Isidro sub-basin of the central Precordillera (Figs 1 and 3). Thin sections were pointed-counted using the Gazzi-Dickinson method (Ingersoll et al., 1984) to minimize grain size effects on the detrital modes. A total of 400 points were counted for each thin section, including monomineralic grains, lithic

fragments, and interstitial cements (see Table S1 in *Supplementary Material*). Texturally, all sandstones are arenites (Pettijohn *et al.*, 1987), with only trace amounts of interstitial matrix.

Villicum and Guandacol sub-basins

Sandstones sampled from the La Cantera Formation (Villicum sub-basin) and the Las Vacas Formation (Guandacol sub-basin) are Upper Ordovician coarse-grained turbidites representing submarine slope apron facies in a fan-delta depositional environment (Peralta, 1993a; Astini, 1998a). Samples of the La Cantera and Las Vacas Formations (Fig. 3) are well- to moderately sorted, medium-grained quartzolithic sandstone composed of angular to well-rounded framework grains and varving amounts (12–33% intergranular volume) of interstitial cements including carbonate and clay minerals. These rocks contain subequal proportions of quartz (QFL%Q = 47-58%), mainly monocrystalline, and lithic fragments (OFL%L = 33-45%), with lesser plagioclase feldspar (QFL%F = 7-9%). K-feldspar is absent in all three samples. Given the textures of these rocks, the absence of K-feldspar is likely to be a function of provenance rather than a diagenetic overprint. Lithic components are dominated by metamorphic (LmLvLs%Lm = 77-92%) guartz-mica and polycrystalline mica aggregates (slate/phyllite/metasedimentary), with les-(LmLvLs%Ls = 2-16%)ser amounts of sedimentary (siltstone/argillite) and intermediate mafic to microlitic volcanic fragments (LmLvLs%Lv = 6-7%). Traces of dense mineral grains such as zircon, tourmaline and apatite are present in the La Cantera Formation. The Las Vacas and lower La Cantera sandstones are nearly identical (QFL = 47:7:46), while the upper La Cantera, though similar, has lower percentage fragments and more plagioclase lithic (OFL = 58:9:33). The lithic suites within the La Cantera and Las Vacas formations are all very similar in mineralogy and texture. This, combined with the absence of potassium feldspar and the presence of quartz grains with vermicular chlorite inclusions, suggests that the formations had a similar provenance. All three quartzolithic sandstones fall within the recycled orogen field of Dickinson (1985) in Fig. 4. Their composition is consistent with a mixed plutonic (feldspar/ quartz), metamorphic, sedimentary, and (minor) volcanic source terrain, similar to the lithologies found in associated conglomeratic and debris flow beds. It is noted that clasts of both mafic volcanic and plutonic rock are observed from the



Fig. 4. QFL diagram for Middle and Upper Ordovician quartzolithic and quartzose sandstones, indicating recycled orogenic, craton interior and transitional continental sources. The four Upper Ordovician sandstones (LV, LLC, ULC, EMP) form a single trend between lithic rich and lithic poor, feldspar poor sandstones. The Middle Ordovician sample (ESI) is a lithic poor sandstone with abundant K-spar, indicating influence from nearby plutonic sources. Q = total quartz (Qp + Qm); F = total feldspar (K + P); L = total lithics (Lt = Lm + Lv + Ls). All samples have a lithic population dominated by metamorphic fragments. Numbers refer to numbered localities in Fig. 1.

Las Vacas and the La Cantera formations (Peralta, 1993a; Astini, 1998a; Keller, 1999), consistent with the presence of intermediate/mafic sand-sized debris in thin section, further supporting a similar provenance for the two formations.

San Isidro sub-basin

A sandstone sampled from the newly defined Estancia San Isidro Formation (ESI) of Darriwilian (early Mid Ordovician) age (P. distichus zone) represents an interval marked by several metres of green shale and thin sandstones above an olistostromal unit that contains the Middle Cambrian San Isidro olistolith and the Upper Cambrian-Lower Ordovician La Cruz olistolith (Heredia & Beresi, 2004). An unconformity at the base of the overlying Empozada Formation of early Late Ordovician age (C. bicornis zone) leads into dominantly black graptolitic shales of the Lower Member of the Empozada Formation (Fig. 3), where a sandstone was sampled from the lower part representing a deep basin facies (Heredia & Beresi, 2004). Sample ESI (Darriwilian) is a very well-sorted, medium- to coarse-grained quartzose

sandstone composed of well-rounded detrital framework and intrabasinal phosphatic grains diversely cemented (25% intergranular volume) by a mixture of quartz, carbonate, Fe-oxide, feldspar and clay minerals. Monocrystalline quartz is dominant with lesser feldspar and minor lithic fragments (QFL = 72:26:2). K-feldspar dominates over plagioclase (P/F = 0.30) and the lithic components are mainly metamorphic (quartzmica tectonite). Volcanic lithic fragments are absent. Sample ESI falls within the transitional continental block field in Fig. 4. Sample EMP (lower Upper Ordovician), by contrast, is a quartzose sandstone with no K-feldspar. Like ESI, it has a very well-sorted, medium-grained framework of rounded to well-rounded framework grains cemented (37% intergranular volume) by a mixture of quartz, Fe-oxide, feldspar, and clay minerals with some bitumen. The dominant framework grains (QFL = 84:14:2) are monocrystalline quartz and plagioclase feldspar with rare, mainly metamorphic (quartz-mica tectonite) lithic fragments. Traces of detrital zircon and tourmaline were noted but not counted. Sample EMP falls within the craton interior provenance field in Fig. 4.

The two sandstones from the San Isidro subbasin are quite different in composition, both from each other, and from the other three described above, likely reflecting differences in age, source and depositional environment. Both of the San Isidro sub-basin sandstones (ESI and EMP) are more feldspathic and have much smaller lithic populations than those at Don Braulio Creek, Villicum sub-basin (ULC and LLC) and at Guandacol (LV) to the north. On the other hand, the Middle Ordovician sandstone (ESI) is also distinguished from the Upper Ordovician sandstones by its high K-feldspar content (QmKP%K = 20%). The four Upper Ordovician K-feldspar-free sandstones fall on a single welldefined trend on the QFL ternary plot between lithic-rich and lithic-poor (quartz rich) compositions (Fig. 4). All four (EMP, LV, ULC, LLC) occur within two successive graptolite zones (the zones of N. gracilis and C. bicornis) that compose the lower Upper Ordovician of the eastern and central Precordillera. Sample EMP, when compared with the La Cantera and Las Vacas samples to the north, is a more texturally mature rock, very well sorted, with rounded to well-rounded grains. Based on its composition and texture, it could conceivably be either partly re-worked from the Las Vacas or La Cantera Formations, or be derived from similar source rocks.

U-Pb Detrital zircon ages and provenance of sandstones

U-Pb relative age probability curves for zircons from the five sandstones described above are shown in Fig. 5. Pb/U concordia age plots for the same samples are shown in Fig. 6, with error ellipses calculated at the 1-sigma level (data and methods available in Table S2 in Supplementary *Material*). The four Upper Ordovician sandstones vield complex U-Pb zircon age spectra characterized by primary peaks in the 1.05-1.10 Ga age range. The Las Vacas sample (Guandacol subbasin) has prominent peaks also at 1.22, 1.30 and 1.46 Ga, which overlap smaller secondary peaks in the other Upper Ordovician sandstones (Fig. 5). Out of a total of 343 zircons analysed from the four Upper Ordovician samples, only three Archaean ages (<1%) are recorded: one concordant 2.6 Ga zircon in the lower La Cantera (Villicum sub-basin), one discordant 2.6 Ga zircon and one concordant 2.7 Ga zircon in the Las Vacas (Fig. 6). Approximately 2.2 Ga zircons are also present in the Las Vacas and Empozada Formation sandstones (one each). Except for the single Archaean zircon and the two ca 1.8 Ga grains in the lower La Cantera, no other zircons older than 1.6 Ga are recorded for the La Cantera

Formation (n = 164). The Upper Ordovician Empozada Formation (San Isidro sub-basin) is likewise characterized by a paucity of zircons older than 1.60 (the *ca* 2.2 Ga grain being the lone exception). Compared with the other Upper Ordovician samples, the Las Vacas Formation contains the most grains (*ca* 10%) in the >1.60 Ga range.

The Middle Ordovician Estancia San Isidro Formation (San Isidro sub-basin) is exceptional for this data set, with its two well-defined peaks at 1·41 and 1·43 Ga, and absence of grains in the 600–1200 Ma range. Aside from two zircons younger than 600 Ma (471 ± 23 Ma; 529 ± 7 Ma), it contains no other zircons younger than 1·20 Ga, and no zircons older than 1·70 Ga. By comparison, the Upper Ordovician samples (except for the lower La Cantera sample) have a minor but significant population of concordant zircons in the 600–700 Ma range (n = 6).

Villicum and Guandacol sub-basins

Not surprisingly, the upper and lower La Cantera samples (Villicum sub-basin) are very similar to each other (Fig. 5). The main difference is that the upper La Cantera is shifted slightly towards younger ages, with 614 ± 5 and 645 ± 6 Ma grains (one each) and no zircons older than 1.50 Ga; in

Fig. 5. Detrital zircon age relative probability curves for five sandstones analysed in this study. Age curves (histograms) are generated by summing the age probability of all analyses per given sample, assuming normal error distribution (Ludwig, 2001), thereby imparting more information than standard histograms. Each curve incorporates age and uncertainty for each grain analysed, plotted as a normal probability distribution. Curves are summed and normalized according to the number of grains, so that each curve contains the same area (Stewart et al., 2001; Gehrels et al., 2003). Ages used are based on ²⁰⁷Pb/²⁰⁶Pb ages and ²⁰⁶Pb/²³⁸U ages for >1 Ga and <1 Ga samples, respectively. Numbers refer to stratigraphic section localities in Fig. 1.



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Fig. 6. Detrital zircon concordia plots for the five sandstones analysed in this study. Grains with >10% discordance were not included. Numbers refer to numbered localities in Fig. 1.

contrast, the lower La Cantera has no grains younger than 950 Ma, and several grains older than 1.50 Ga (n = 5). The single Las Vacas Formation sample (Guandacol sub-basin; n = 86) is almost identical to the combined age spectra for the two La Cantera Formation samples (n = 164). Besides the obvious overlap of peaks between 1.0 and 1.5 Ga (Fig. 5), the Las Vacas Formation also contains 656 ± 20 and 691 ± 21 Ma grains. The main difference is in the larger proportion of Las Vacas zircons (13%) older than 1.50 Ga. Based on these data, the detrital zircon age spectra appear to strongly reinforce field observations, stratigraphic and petrographic data that interpret the Las Vacas and La Cantera Formations as having a near-identical provenance. Furthermore, the siliciclastic source is probably composed in part of a terrane dominated by recycled basement components in the 950 Ma to 1.5 Ga age range. It is inferred from this that the main population of granitic and orthoquartzite clasts in the conglomerates of these formations probably represents the same age distributions. Lack of grains younger than 600 Ma reinforces petrographic data indicating that Ordovician volcanic arc sources, such as those that produced the K-bentonites in the upper San Juan Formation, were not shedding significant zircon-bearing material directly into these sedimentary basins. The rare volcanic grains recognized in thin sections of these sandstones are therefore probably older than 600 Ma, or are not associated with any detectable zircon.

San Isidro sub-basin

The Upper Ordovician Empozada Formation (n = 93) reveals a similar age spectrum to the combined Upper Ordovician La Cantera/Las Vacas (n = 250) zircon age population, with most ages concentrated in the 950 Ma to 1.5 Ga age range (Fig. 5). Like the combined La Cantera/Las Vacas data, the Empozada Formation (EMP) has zircons in the 600-700 Ma range (647 ± 5 and 703 ± 10 Ma), with a few scattered ages also between 950–870 Ma (nine grains), but none younger, indicating very similar sources, as suggested by petrographic data. A strong ca 1.40 Ga secondary peak is the only one overlapping that of the underlying Estancia San Isidro Formation (ESI) at this locality, which also contains the two youngest zircons of the five sandstones (471 ± 23) 529 ± 7 Ma). These contrasting spectra suggest a very different provenance for samples from the Middle Ordovician Estancia San Isidro Formation (n = 73). This is consistent with petrographic data, which indicate proximal basement/plutonic sources, an observation reinforced by the narrow range of ages in the ESI zircon age spectrum (>95% 1200-1600 Ma), indicative of a more proximal (or point) source for this sample.

Sm-Nd isotopic composition of graptolitic shales

Thirty-two Middle and Upper Ordovician graptolitic shale samples collected from six separate localities were analysed for their whole-rock Sm-Nd isotopic composition in order to further constrain the provenance of siliciclastic sediment sources in the Precordillera. Results are shown in Table 1. Nd isotopic compositions were re-calculated for stratigraphic age and expressed as initial $\varepsilon_{\rm Nd}$ values, which are emphasized over model ages ($T_{\rm DM}$) for reasons enumerated in Gleason *et al.* (1994, 1995, 2002). All initial (age-corrected) $\varepsilon_{\rm Nd}$ values are calculated at 450 Ma for consistency. Although the total age range of our samples is *ca* 465 Ma to *ca* 444 Ma, any resulting offset in the initial $\varepsilon_{\rm Nd}$ for samples recalculated for their precise stratigraphic age is <0.20 epsilon units.

The total range of $\varepsilon_{Nd}(450)$ for the combined Precordillera Middle and Upper Ordovician dataset is -9.6 to -4.5. The average $\varepsilon_{Nd}(450)$ of Upper Ordovician rocks is $\varepsilon_{\rm Nd} = -6.2 \pm 0.9$ (1-sigma of the total population), with average $T_{\rm DM} =$ 1.51 ± 0.15 Ga (Fig. 7). At Don Braulio Creek (Villicum sub-basin) (Fig. 8), values hardly vary at all upsection $[\epsilon_{Nd}(450) = -6.5 \pm 0.3; T_{DM} =$ 1.53 ± 0.05 Ga; n = 6], starting with the upper Middle Ordovician Gualcamavo Formation (Darriwilian) through the lower Upper Ordovician La Cantera Formation (5th stage) into the Hirnantian-age (upper Upper Ordovician) Don Braulio Formation. In the Guandacol sub-basin (Fig. 8), six samples representing the lower Middle through Upper Ordovician succession (Gualcamayo and Las Vacas formations) yield a similar pattern $[\varepsilon_{\rm Nd}(450) = -6.9 \pm 0.3;$ $T_{\rm DM} = 1.57 \pm 0.15$ Ga; n = 6]. The base of the Gualcamayo Formation at this locality is older (lower Middle Ordovician) by two graptolite zones than the Gualcamayo Formation elsewhere in the Precordillera (Astini, 2003), but samples are from younger strata coeval with other localities. The five samples of Gualcamayo Formation analysed from the Guandacol sub-basin $[\varepsilon_{\rm Nd}(450) = -7.0 \pm 0.3; n = 5]$ are very similar to the three samples of the Gualcamayo Formation analysed from the Villicum sub-basin [$\varepsilon_{Nd}(450)$ - -6.6 ± 0.4 ; n = 3] (Fig. 8), indicating very little regional variation. A single Gualcamayo Formation age-equivalent sample from Cerro La Chilca (San Juan sub-basin) has $\varepsilon_{Nd}(450)$ of -7.4. The total range of variation and mean value for the Gualcamayo Formation in the Precordillera Terrane obtained from this study is $\varepsilon_{\rm Nd}(450) = -6.9 \pm 0.4$ $(T_{\rm DM} = 1.57 \pm 0.12 \text{ Ga}; n = 9).$

At Cerro La Chilca (San Juan sub-basin), there is a significant offset between the Middle Ordovician siliciclastics of the San Juan Formation/ Gualcamayo Formation condensed sequence $[\varepsilon_{\rm Nd}(450) = -7.5 \pm 0.2;$ $T_{\rm DM} = 1.58 \pm 0.02$ Ga; n = 3] and the lower Upper Ordovician Los Azules Formation [$\varepsilon_{Nd}(450) = -5.1 \pm 0.5$; $T_{DM} =$ 1.47 ± 0.02 Ga; n = 4](Fig. 8). At San Isidro Creek (San Isidro sub-basin), a shift in isotopic composition is also observed between the Darriwilian Estancia San Isidro Formation $[\varepsilon_{Nd}(450)]$ - -8.6 ± 0.9 ; T_{DM} = 1.67 ± 0.07 Ga; n = 3] and the lower Upper Ordovician Empozada Formation $[\varepsilon_{\rm Nd}(450) = -6.1 \pm 0.4;$ $T_{\rm DM} = 1.41 \pm 0.07$ Ga; n = 4]. The more negative $\varepsilon_{\rm Nd}$ of the Estancia San Isidro Formation also appears to be reflected by older detrital zircons (average = 1408 Ma ESI vs. 1189 Ma EMP). Nd isotopic analysis of conodonts from the Empozada Formation yielded $\varepsilon_{\rm Nd}(450)$ of -5.9 (Wright *et al.*, 2002), identical to that of the siliciclastic host (Fig. 8).

Contained within this data set are some interesting stratigraphic trends. $\varepsilon_{Nd}(450)$ becomes less negative upsection at the La Chilca section of the San Juan sub-basin (Fig. 8), where a positive shift in $\varepsilon_{Nd}(450)$ is accompanied by an increase in clastic sediment supply across a stratigraphic paraconformity. At the San Isidro section (San Juan sub-basin), a trend towards more negative values upsection in the Upper Middle Ordovician Estancia San Isidro Formation is replaced by less negative $\varepsilon_{Nd}(450)$ of the Lower Upper Ordovician Empozada Formation above a paraconformity (Fig. 8). By contrast, $\varepsilon_{\rm Nd}(450)$ for the Ordovician of the Villacum and Guandacol sub-basins is quite homogeneous upsection from Middle through Upper Ordovician stratigraphic levels (Fig. 8). Another observation also deserves comment: the Upper Ordovician Pavón Formation, from the San Raphael area of the southernmost Precordillera Terrane (correlated with rocks of the western basins by Astini, 2003), records a significantly more positive $\epsilon_{\rm Nd}(450)$ of -2.9 ± 1.4 ($T_{\rm DM}=$ 1.38 ± 0.16 Ga; n = 5; Cingolani *et al.*, 2003) compared with any of the Precordillera Ordovician siliciclastics analysed here.

Very limited sampling in the western basins yielded four analyses of black shale from the Hirnantian-age Alcaparrosa Formation [$\varepsilon_{Nd}(450) =$ $-6\cdot8 \pm 0\cdot4$; $T_{DM} = 1\cdot64 \pm 0\cdot18$ Ga; n = 4]. These values overlap with the Precordillera Upper Ordovician average ($\varepsilon_{Nd} = -6\cdot2 \pm 1\cdot0$). A single Upper Ordovician data point (lower Upper Ordovician; *N. gracilis* Zone) from the Yerba Loca Formation [$\varepsilon_{Nd}(450) = -8\cdot1$] is the most negative value measured in the Upper Ordovician siliciclastic rocks from the Precordillera (YL-1; Table 1). A Middle Ordovician (Darriwilian; *P. tentaculatus* Zone) sample (YL-3) from the

	4		Strat.)	British		¹⁴³ Nd/ ¹⁴⁴ Nd			147 Sm/		$T_{\rm DM}$
Sample	Locality	Formation	position	Stage	series	Graptolite zone	measured	2 SD	$\varepsilon_{ m Nd}(0)$	¹⁴⁴ Nd	$\varepsilon_{\rm Nd}(t)$	(Ga)
VR-1	Villicum	Gualcamayo	base	Darriwilian	Llanvirn	P. tentaculatus	0.512054	$\frac{12}{2}$	-11.4	0.1193	6·9–	1.59
VK-1 replicate	Willicium	Gualcamaxo	10.4 m	Darritari	Ilanzim	D tentaculatus	0.512068 0.512080	9 1 10	-11.1 -10.0	0.1200	2.9-	1.60 1.61
VR-11 VR-11	Villicum	Gualcamayo	89·5 m	Darriwilian	Llanvirn	P. tentaculatus	0.512091	12	-10.7	0.1185	-6.2	1.52
VR-16	Villicum	La Cantera	Base	5th	Caradoc	N. gracilis	0.512090	12	-10.7	0.1158	0.9-	1.48
VR-23	Villicum	La Cantera	Top	5th	Caradoc	N. gracilis	0.512063	11	-11.2	0.1136	-6.4	1.49
VR-25	Villicum	Don Braulio	Base	Hirnantian	Ashgill	N. extraordinarius	0.512064	11	-11.2	0.1156	-6.5	1.51
LC-H clay	La Chilca	San Juan	Upper	3rd	Arenig		0.512056	6	-11.4	0.1279	-7-4	1.74
LC-FSJ clay	La Chilca	San Juan	Upper	3rd	Arenig		0.511956	17	-13.3	0.1001	-7.8	1.45
LC-1	La Chilca	Gualcamayo	Base	Darriwilian	Llanvirn	P. tentaculatus	0.512012	12	-12.2	0.1132	-7-4	1.56
LC-1 replicate							0.512003	18	-12·4	0.1135	-7.6	1.57
LC-8	La Chilca	Los Azules	Base	5th	Caradoc	N. gracilis	0.512173	11	-9.1	0.1385	-2.7	1.75
LC-9	La Chilca	Los Azules	Top	5th	Caradoc	N. gracilis	0.512133	13	6.6-	0.1170	-5.3	1.43
LC-11	La Chilca	Los Azules	Near top	5th	Caradoc	N. gracilis	0.512165	12	-9.2	0.1203	-4.8	1.43
LC-12	La Chilca	Los Azules	Near base	5th	Caradoc	N. gracilis	0.512137	12	-9.8	0.1052	-4.5	1.27
SI-1	San Isidro	Est. San Isidro	1.0 m	Darriwilian	Llanvirn	P. distichus	0.512024	14	-12.0	0.1251	-7-9	1.74
SI-2	San Isidro	Est. San Isidro	11.0 m	Darriwilian	Llanvirn	P. distichus	0.511977	12	-12.9	0.1160	-8·3	1.65
SI-3	San Isidro	Est. San Isidro	21·0 m	Darriwilian	Llan./Car.	P. distichus	0.511872	6	-14.9	0.1035	9.6 -	1.61
SI-4	San Isidro	Empozada	31·0 m	5th	Caradoc	C. bicornis	0.512066	11	-11.2	0.1121	-6.3	1.46
SI-5	San Isidro	Empozada	41.0 m	5th	Caradoc	C. bicornis	0.512093	14	-10.6	0.1065	-5.4	1.34
SI-6	San Isidro	Empozada	51.0 m	5th	Caradoc	C. bicornis	0.512077	11	-10.9	0.1149	-6.2	1.48
SI-7	San Isidro	Empozada	68·0 m	5th	Caradoc	C. bicornis	0.512027	10	-11.9	0.1007	-6.4	1.37
SI-7 replicate							0.512043	11	-11.6	0.1003	-6.1	1.34
C-1	Calingasta	Alcaparrosa	0·0 m	Hirnantian	Ashgill	N. extraordinarius	0.512095	10	-10.6	0.1301	-6.8	1.72
C-2	Calingasta	Alcaparrosa	2.0 m	Hirnantian	Ashgill	N. extraordinarius	0.512019	11	-12.1	0.1065	6.9-	1.45
C-2 replicate					;		0.512011	12	-12.2	0.1034	6.9-	1.42
C-3	Calingasta	Alcaparrosa	4·0 m	Hirnantian	Ashgill	N. extraordinarius	0.512083	11	-10.8	0.1184	-6.3	1.53
C-4	Calingasta	Alcaparrosa	8·0 m	Hirnantian	Ashgill	N. extraordinarius	0.512080	13	-10.9	0.1347	-7·3	1.84
YL-1	Rio Jachal	Yerba Loca	Roadcut	5th	Caradoc	N. gracilis	0.512212	16	-8·3	0.1928	-8.1	I
YL-3	Rio Jachal	Yerba Loca	Tunnel	Darriwilian	Llanvirn	P. tentaculatus	0.511936	14	-13.7	0.0982	-8.0	1.45
01-SF-I-9	Guandacol	Las Vacas	Base	5th	Caradoc	C. bicornis	0.512072	12	-11.0	0.1176	-6.5	1.53
01-SF-1-11	Guandacol	Gualcamayo	182 m	Darriwilian	Llanvirn	P. tentaculatus	0.512075	10	-11.0	0.1337	-7-4	1.83
01-SF-1-12	Guandacol	Gualcamayo	165 m	Darriwilian	Llanvirn	P. tentaculatus	0.512023	11	-12.0	0.1013	-6.5	1.38
01-SF-I-14	Guandacol	Gualcamayo	120 m	Darriwilian	Llanvirn	P. tentaculatus	0.512057	6	-11·3	0.1214	-7.0	1.62
01-SF-I-17	Guandacol	Gualcamayo	00 m	Darriwilian	Llanvirn	P. tentaculatus	0.512042	11	-11.6	0.1123	-6.8	1.50
01-SF-I-19	Guandacol	Gualcamayo	30 m	Darriwilian	Llanvirn	P. tentaculatus	0.512033	12	-11.8	0.1149	-7.1	1.55
01-SF-I-19 rep1							0.512024	12	-12.0	0.1117	-7.1	1.52
01-SF-I-19 rep2							0.512022	11	-12.0	0.1113	-7-1	1.51
Amoin C concert	man lound this	143NIA /14	NId notic is 19 v	w 66.0+) w u	(otinu notito)							
Average 2-sigina 1 a rolla Nd stand	internal prec הייל (ה – 27)	1810N 0N ' '' NU/ — 0.511840 + 0.00	r Nd ratio is iz p ا 2 Simma (مناسبة	.p.m. (±u 23 e]	psilon units).							
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Average external	reproducibili	ity of Sm/Nd ratio	based on replica	ate analyses is	±1%.			m undo				
Uncertainty on S	m-Nd model	ages (DePaolo, 19	81) is ±1%.		• • • • •							
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 Table 1. Nd isotopic composition of Ordovician graptolitic shales, Argentine Precordillera

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Fig. 7. Nd isotopic variation of Upper Ordovician samples (see text). The horizontal double line is the mean of the entire population of Upper Ordovician samples measured [$\varepsilon_{\rm Nd}(450) = -6.2$; n = 17], with a standard deviation (1-sigma) of one epsilon unit.

Yerba Loca Formation is the same, within error $[\epsilon_{\rm Nd}(450) = -8.0]$.

These limited data confirm that the outer slope/ basinal facies of the western Precordillera received siliciclastic material from broadly similar sources as the eastern basins; however, the more negative values in the Yerba Loca Formation could hint at a slightly different mix of sources between the two settings. Because units sampled from the western basins represent a tectonic mélange, the data must be used with caution. The extreme degree of tectonic deformation and chaotic sedimentation within the Yerba Loca Formation does not eliminate the possibility that, although graptolite ages were assigned at these outcrops and refined later in the laboratory from the collected samples, they may still not be representative of the material analysed for Nd isotopes. It is perhaps not surprising that, given the degree of hydrothermal metamorphism and deformation experienced by rocks in the western basin, Sm/Nd ratios show maximum variation here (Table 1), reinforcing the need for caution when interpreting Nd model ages. Fig. 9 reveals the close dependence upon Sm/Nd ratios of calculated model ages in this data set. The two samples of the Yerba Loca Formation, which show maximum Sm/Nd ratio variation and identical initial ratios at 450 Ma, produce a 445 Ma two-point whole-rock isochron, consistent with a late Ordovician/early Silurian age for regional deformation and metamorphism.

Common Pb isotopic composition of graptolitic shales

Fifteen Middle and Upper Ordovician graptolitic shale samples representing six separate localities

in the Precordillera were analysed for their whole-rock Pb isotopic composition in order to complement the provenance information from the Nd isotopes. Results are shown in Table 2. On a ²⁰⁷Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb uranogenic Pb-Pb isotope plot (Fig. 10), the Precordillera samples form a linear array trending towards values typical of radiogenic crust (Stacey & Kramers, 1975). Pb data from the Precordillera basement (Kay et al., 1996; corrected to the same isotopic standard values used in the present study - see Methods in Appendix S1, in Supplementary Material) are shown, along with data fields for other relevant sample sets. From these comparisons, it appears that Precordillera Ordovician shales were derived from sources with elevated ²⁰⁷Pb/²⁰⁴Pb for a given range of ²⁰⁶Pb/²⁰⁴Pb relative to Precordillera basement (Fig. 10). Employing the methods used in Tohver et al. (2004), model mu-values $(\mu_2 = {}^{238}\text{U}/{}^{204}\text{Pb})$ were calculated for all 15 samples assuming an average time of removal from their source terrane(s). Using this approach, the Precordillera Ordovician shales yield a highly uniform cluster of model μ_2 (T = 1.0 Ga) values with an average $\mu_2 = 9.8 \pm 0.1$ (n = 15), which is less radiogenic than the model μ_2 (T = 1.0 Ga) calculated Precordillera for basement $(\mu_2 = 9.4 \pm 0.1; n = 4)$. The Precordillera shales yield a statistically tight cluster of values that likely represent a mixture of source terranes, transitional in their Pb isotope evolution between average Grenvillian-age basement typical of Laurentia ($\mu_2 = 9.5$), and Grenvillian-age basement provinces more typical of the Amazon craton $(\mu_2 = 10.0; \text{ Tohver } et al., 2004).$

The above analysis receives some confirmation from the fact that calculated model $\varepsilon_{Nd}(1.0 \text{ Ga})$ values, filtered for ${}^{147}\text{Sm}/{}^{144}\text{Nd} < 0.14$ (e.g. Tohver et al., 2004), show a fairly narrow range of initial ε_{Nd} (-1.0 ± 1.2) for Precordillera Ordovician rocks. which appears transitional between the Laurentian Grenville Prov- $[\varepsilon_{\rm Nd}(1.0 \text{ Ga}) = +3]$ ince and Amazonian Grenvillian-age domains, which may also include parts of the allochthonous Appalachian Blue Ridge province of North America $[\varepsilon_{Nd}(1.0 \text{ Ga}) = -4;$ Tohver *et al.*, 2004]. The Pb-Pb isotope trend for the Precordillera Ordovician shales also yields an apparent secondary (pseudochron) age of *ca* 490 Ma. Despite the near-coincidence of this apparent Pb-Pb age with the depositional age, the above-cited Sm-Nd whole-rock isochron, and that of Precordilleran K-bentonites, caution must be exercised in any interpretations. Efficient mixing of sedimentary

Eastern and Central Precordillera



Fig. 8. Nd isotopic variations for each sampled stratigraphic section (see text). Numbers refer to section locations in Fig. 1. Sandstone sample positions (petrography and U-Pb detrital zircon geochronology) are indicated by an asterisk. Conodont values from Empozada Formation from Wright *et al.* (2002).

components between different sources is just as likely to yield a mixing array of this slope, and therefore these two end-member possibilities cannot be distinguished on this basis alone.

INTERPRETATION OF PROVENANCE

The data presented here are interpreted as reflecting a mixed provenance for the Precordilleran Ordovician siliciclastic succession that includes: (1) Precordillera basement, (2) Cambrian siliciclastic facies, and (3) an unidentified terrane (or terranes) with a high- μ Pb isotope affinity. The first two are consistent with previous work documenting proximal Precordillera platform and basement sources for the Precordillera Ordovician succession, while the third component is mainly inferred from the Pb isotopic composition of the shales.

Meta-quartzites and schists from exposed basement in the Sierra de Pie de Palo (Fig. 1) have a similar zircon age population (1150–1160, 1050– 1080 and 665 Ma; Vujovich *et al.*, 2004) as detri-



Fig. 9. Nd model age vs. Sm/Nd. The strong correlation between these parameters suggests caution in the use and interpretation of Nd model ages to infer provenance information.

tal zircons in Upper Ordovician Sandstones, reinforcing previous suggestions that the Pie de Palo basement complex and cover could have been one of the sources of the Precordillera Upper Ordovician clastics (Astini, 2003). Middle Cambrian Precordillera platform siliclastic facies, as well as olistoliths containing Middle Cambrian platform siliciclastic facies (e.g. San Isidro Olistolith), have zircon age populations that overlap with the Ordovician detrital zircon data set (Finney *et al.*, 2005), reinforcing stratigraphic evidence for a significant recycled platform sediment component. Lower Cambrian siliciclastics at the base of the Precordillera carbonate platform (Cerro Totora Formation) also contain abundant 1.0–1.5 Ga detrital zircons (Thomas et al., 2004; Finney, 2006), similar to the Middle and Upper Ordovician siliciclastic succession studied here. Finally, granitic clasts from Ordovician conglomerates directly overlying Mesoproterozoic basement of the San Raphael Block have a uniform population of 1.2 Ga zircons (Finney, 2006), while granitic clasts from a conglomerate in the Lower Member (lower Upper Ordovician) of the Empozada Formation (San Isidro sub-basin) are dominantly ca 1.4 Ga in age (Finney, 2006). These observations all support a significant component of recycled basement and lower platform sources in the Precordillera Middle and Upper Ordovician siliciclastic succession, consistent with stratigraphic analysis and sandstone petrography.

A strong component of cannibalistic recycling is evident upsection in the eastern Precordillera Ordovician siliciclastic succession, where angular clasts of Gualcamayo Formation and San Juan Formation are incorporated into debris flows of early Late Ordovician age (Thomas *et al.*, 2002; Astini, 2003). The neodymium isotopic data show that, in these parts of the Precordillera, sediment sources were isotopically well-mixed for Middle through Upper Ordovician siliciclastic rocks (Villicum and Guandacol sub-basins). At other localities (San Isidro and San Juan sub-basins), there is a significant shift in the neodymium isotopic composition between the Middle and

Sample	²⁰⁸ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb
VR-1	39·2329	15.7178	19.7011	1.99138	0.797814
VR-2	39.2947	15.7213	19.7095	1.99367	0.797673
VR-16	38.9043	15.6511	18·8863	2.05990	0.828715
VR-23	38.8434	15.6557	18·9241	2.05249	0.827274
C-1	38·9789	15·9067	23.3274	1.67087	0.681865
C-2	38.7578	15·7762	20.8504	1.85877	0.756604
YL-1	38·7761	15.7999	21.3057	1.82001	0.741583
YL-2	38·9239	15.7059	20.2176	1.92513	0.776855
LC-11	39·0127	15.6983	19.5154	1.99916	0.804495
LC-12	38·6162	15.6761	19.4358	1.98687	0.806553
SI-5	38.8485	15.8203	21.5649	1.80145	0.733632
SI-7	38.5374	15·7571	20.3923	1.88970	0.772678
SF-I-11	38·5128	15.6830	19.0861	2·01780	0.821702
SF-I-12	39.4630	15.7220	19.8114	1.99192	0.793637
SF-I-19	38·7016	15.6754	19.0022	2.03670	0.824927
replicate	38.7046	15.6762	19.0048	2.03651	0.824861

Table 2. Common Pb isotopic composition of Precordillera Ordovician shales.

Mass 202 monitored for Hg interference.

All ratios normalized by internal Tl correction (corrected to NBS-981values of Todt et al., 1996).

Reproducibility estimated as follows: ${}^{208}\text{Pb}/{}^{204}\text{Pb} = \pm 0.010\%$; ${}^{207}\text{Pb}/{}^{204}\text{Pb} = \pm 0.008\%$; ${}^{206}\text{Pb}/{}^{204}\text{Pb} = \pm 0.013\%$; ${}^{208}\text{Pb}/{}^{206}\text{Pb} = \pm 0.006\%$; ${}^{207}\text{Pb}/{}^{206}\text{Pb} = \pm 0.004\%$.



Fig. 10. Present-day uranogenic Pb-Pb isotope plot. Precordillera Ordovician siliciclastic material appears to be transitional between Precordillera basement (Kay *et al.*, 1996) and Gondwanan crust of the Proterozoic Amazon craton (Tohver *et al.*, 2004). Southern Puna Ordovician clastics derived from the Arequippa Massif of Bolivia (Egenhoff & Lucassen, 2003) are also shown for reference. S-K represents the second stage crustal evolution curve of Stacey & Kramers (1975).



Fig. 11. Nd isotope ranges (1 standard deviation of the population) for Precordilleran Ordovician siliciclastic rocks measured in this study, and for the San Raphael area (Pavón Formation; Cingolani *et al.*, 2003), arranged by sub-basin. The San Isidro and San Juan subbasins show a change in isotopic composition between Middle and Upper Ordovician units, while the Villicum and Guandacol sub-basins do not. The Gualcamayo Formation and the western Precordillera basins are also singled out for comparison.

Upper Ordovician assemblages (Fig. 11). Within the eastern and central basins (excluding the western Precordillera), the data converge on a fairly uniform signature for the Upper Ordovician $[\varepsilon_{\rm Nd}(450) = -5.9 \pm 0.4;$ $T_{\rm DM} = 1.46 \pm 0.12$ Ga; n = 12], suggesting a regional trend towards greater isotopic homogeneity and mixing of sources upsection. An exception to this (Fig. 11) is the data set collected by Cingolani *et al.* (2003), for which Upper Ordovician (Caradocian) turbidites of the Pavón Formation in the southernmost Precordillera Terrane (San Raphael sub-basin) yielded a less negative $\varepsilon_{\rm Nd}(450) = -2.9 \pm 1.4$ $(T_{\rm DM} = 1.38 \pm 0.16$ Ga; n = 5). Cingolani *et al.* (2003) interpreted the source of these greywackes to be dominantly Grenville-age crust, with an additional contribution from a mature (e.g. Famatinian) magmatic arc.

Although an eastern volcanic arc source, possibly represented by the Famatina Arc, has been proposed for the Ordovician siliciclastic succession of the Precordillera (e.g. Astini *et al.*, 1995). there is little direct evidence for this in the samples studied here. Aside from *ca* 470 Ma K-bentonites preserved in the upper San Juan Formation (and in the oldest part of the Ordovician Gualcamayo Formation of the eastern basins). there is little evidence for a significant juvenile volcanic component in the Precordillera Ordovician siliclastic succession. Only 1 of 416 zircons (<0.3% of the total) analysed here has an age that could be considered Famatinian (471 ± 23 Ma; Estancia San Isidro Formation). Lack of direct evidence for sediment sources in the Famatina Arc indicates that either (1) a more distant location for the Precordillera at this time is required, or (2) that more local sources dominated at all the localities sampled. The data do not rule out the presence of an isotopically evolved (e.g. Famatina-like) crustal component derived from elsewhere along the evolving proto-Andean margin of Gondwana during the Ordovician, as suggested by the Pb isotope data. Based on the 15 Pb whole rock, 32 Nd whole rock, 416 U-Pb detrital zircon, and six sandstone petrographic analyses, it is calculated that anywhere from 5% to 30% of the siliciclastic material could be derived from high-µ Pb isotope sources of Gondwanan affinity (e.g. Schwartz & Gromet, 2004; Tohver et al., 2004). Parts of the Lower and Middle Ordovician Famatina volcaniclastic succession may in fact provide an isotopic match (Nd-Pb work has vet to be carried out on the these rocks). For example, according to the work of Pankhurst et al. (1998), igneous and metamorphic basement rocks of the Famatina Complex (one likely source of the Famatina Ordovician volcaniclastic succession) have an average $\epsilon_{\rm Nd}(450) = -6.0 \pm 0.8$ (*n* = 23). Such values are a close match for Ordovician siliciclastic rocks studied from various other parts of the South American proto-Andean margin (e.g. Bock et al., 2000: Egenhoff & Lucassen, 2003: Zimmermann & Bahlburg, 2003), including the Precordillera Ordovician assemblage studied here (Fig. 12). Most



Fig. 12. Nd isotope range (1 standard deviation of the population) for Ordovician siliciclastic succession of the Precordillera compared with other Ordovician siliciclastic assemblages. Data are from this study, Gleason *et al.* (1994, 1995, 2002), Kay *et al.* (1996), Bock *et al.* (2000), Egenhoff & Lucassen (2003), Zimmermann & Bahlburg (2003) and Dickinson *et al.* (2003). The Nd isotopic composition of Precordillera Ordovician siliciclastic material falls within the range of known Precordillera basement samples (Kay *et al.*, 1996).

workers interpret these isotopic signatures being as representative of mature continental margin arc settings (e.g. Famatina-Puna Ordovician arc), like that of the modern Andean arc (Pankhurst *et al.*, 1998; Bock *et al.*, 2000; Kleine *et al.*, 2004), which incorporate substantial recycled continental crust. The U-Pb detrital zircon data presented here suggest, however, that any such source (i.e. with high- μ Pb) supplying Precordillera Ordovician siliciclastic systems would have been dominated by a zircon population 1·0–1·5 Ga in age.

The assembled data can be used to evaluate, to some extent, the tectonic setting of Precordillera Ordovician basins (Fig. 2). Disintegration of the Precordillera carbonate platform may have occurred along a strike-slip fault system (extensional pull-apart basins; Finney et al., 2005; Finney, 2006), by flexural extension initiated by lithospheric loading of thrust sheets along a subduction zone (Thomas & Astini, 2003), or along a zone of oblique subduction (Benedetto, 2004). Astini (1998a, 2003) and Thomas & Astini (2003) favoured development of a peripheral forebulge that migrated to allow accommodation space for a clastic wedge with eastern sources to develop. This would put the Precordillera in a foreland basin setting during the Middle and Late Ordovician. Keller (1999) favoured an active rift margin setting for the Precordillera Terrane during the Ordovician, though his interpretation of regionally developed breakup- and post-rift unconformities is not considered compatible with current understanding of the Middle and Late Ordovician stratigraphic record of the Precordillera (Finney, 2006). The foreland basin setting favoured by many workers (e.g. Astini et al., 1995; Astini, 1998a) is reinforced, in particular, by the recycled orogen provenance of the sandstones, compatible with paleocurrent data indicating significant transport along basin axes (Astini, 1998a). The Nd isotopic data ($\varepsilon_{Nd} =$ 6.2 ± 1.0 ; $T_{\rm DM} = 1.51 \pm 0.15$ Ga) and the coherent detrital zircon age spectra (ca 1.0-1.5 Ga) in Upper Ordovician rocks indicate increasing regional homogenization of sediment sources as siliciclastic basins evolved atop the Precordillera carbonate platform, consistent with a recycled orogenic provenance. The broad similarities in Nd-Pb isotopic composition between the western and eastern basins, in particular by Late Ordovician time, are also consistent with the hypothesis for a regionally developed (Oclovic) clastic wedge, with recycled orogenic sources lying dominantly to the east (Astini et al., 1995; Astini, 1998a); however, much more work and better agecontrol is necessary in the western basins before this assertion can be tested further with radiogenic isotope provenance tracers.

The scale of regional events that gave rise to the large olistoliths (Mid and early Late Ordovician 'Guandacol' event) and major paraconformities (e.g. missing Middle Upper Ordovician section), persuaded Keller (1999) that these were predominantly extensional basins formed by prolonged rifting starting in the early Mid Ordovician. Keller's geodynamic model follows that of Lowe (1985) for the evolution of the Ouachita margin, from which the Precordillera Terrane is proposed to have been derived (Thomas & Astini, 1996). Lowe (1985) interpreted the Lower Paleozoic Ouachita assemblage as being deposited in a narrow marine trough bounded by an outboard terrane, which Keller (1999) interpreted as being the Precordillera Cambro-Ordovician carbonate platform. Although the Nd data do not rule out the Keller (1999) Ordovician rifting hypothesis, it is noted that the large Nd isotope shift recorded in the Upper Ordovician succession of the Ouachita assemblage of Texas-Oklahoma-Arkansas (Gleason et al., 1994, 1995, 2002) does not appear to be present in the Precordillera. The average post-Nd isotope shift signature (Fig. 12) in the Ouachita assemblage (-8) is somewhat different (with some overlap) from the average Precordillera Upper Ordovician Nd isotopic signature obtained from this study (-6), though this observation does not provide much constraint on paleogeography. The Pb isotopic data do, however, appear to suggest the presence of an additional sediment source in the Precordillera Ordovician succession not accounted for in the Keller (1999) rift model. It is noted that the Appalachian Cambro-Ordovician carbonate platform, which shares many similarities with the Precordillera platform (Bond et al., 1984; Astini et al., 1995), began receiving increased volumes of siliciclastic material during Blountian-stage (early Mid Ordovician) subsidence and collapse, at about the same time that Keller's (1999) proposed rifting event commenced in the Precordillera (Thomas et al., 2002). However, the southern Appalachian siliciclastic material is decidedly less radiogenic [$\varepsilon_{Nd}(460)$] $= -9.2 \pm 0.4$; n = 5] at the base of the Blountian (Gleason et al., 2002) than are the slightly younger siliclastic sediments from the Precordillera that mark the initial drowning of the platform [Darriwilian-age Gualcamayo Formation; $\varepsilon_{Nd}(460)$ $= -6.9 \pm 0.4$; n = 9]. Therefore, the data would seem to permit no communication of siliclastic delivery systems during this time between these independently evolving regions, placing some constraints on the regional extent of dispersal systems if the Keller (1999) hypothesis is correct. Additional Pb-Nd whole-rock isotopic data on the clay component in Precordillera Cambro-Mid Ordovician carbonates would be useful to have in this context.

The interpretations presented here necessarily reflect the many complexities encountered with basin evolution studies in the Precordillera. Isotopic data from overlying Silurian-Devonian strata could be used as a potential test of the pull-apart basin model advocated by Finney (2006). In this context, Loske (1995) found dominantly 1.1 Ga ages for detrital zircons in Devonian graywackes in the western Precordillera, suggesting that recycling of the lower Palaeozoic sedimentary assemblage continued to dominate the sediment supply along the evolving Precordillera margin. Loske (1995), however, favoured a back-arc setting for the western Precordillera basins, comparable with the Ordovician siliciclastic assemblage of the Famatina Basin and its extension into the Puna region of northern Argentina and Bolivia (Zimmermann & Bahlburg, 2003; Kleine et al., 2004), with later emplacement along strike-slip faults. More detailed studies of the Gualcamayo Formation, combining high-resolution graptolite stratigraphy with geochemistry, should provide a clearer picture of the earliest stages of siliciclastic basin evolution in the Precordillera over a broader region than was sampled for this study. The mystery of the clastic

sources for the Gualcamayo Formation remains in part unsolved because of its uniformly finegrained composition.

SUMMARY

As unroofing progressed, the Precordillera platform sequence and underlying (Lower Cambrian) rift-related assemblages (Thomas et al., 2004) probably supplied large amounts of recycled clastic sediment along with nearby Proterozoic basement to the Ordovician basins. Although terranes lying outboard of the Precordillera terrane may also have supplied sediment, a juvenile isotopic component is not detected in the zircon ages or Nd isotopic signatures reported here. While this could still be compatible with sources in the Famatina Arc (based on overlapping Nd isotopes), the lack of Ordovician-age zircons in the Precordillera Ordovician assemblage (other than from bentonite beds), suggests that any material from such a source evolved (i.e. felsic) enough to carry zircons did not reach these basins. From the data presented here, the proximity of such a terrane must remain an inference, based mainly on the Pb isotopic data of the finegrained material only, which was interpreted by Astini (1998a, 2003) to have had sources external (extra-basinal) to Precordillera Mid and Late Ordovician basins. The delay, or lag-time, required for juvenile components from accreted arc terranes to become a significant source in continental margin foreland basin assemblages is well known (e.g. McLennan et al., 2001), sometimes requiring more than one orogenic cycle.

Detrital zircon ages in the Precordillera Ordovician siliciclastic assemblage which do not seem to fit a Laurentian provenance (e.g. Rapela et al., 1998b; Sims et al., 1998; Schwartz & Gromet, 2004) include 2.2 Ga (two grains) and 600-700 Ma (four grains), which are lacking in Cambrian clastic units (Finney et al., 2005), except for a 615 Ma grain in the sandstone of the Middle Cambrian San Isidro Olistolith (Finney et al., 2005); however, these ages make up only 2% of all grains analysed in the Ordovician succession. One young grain $(471 \pm 23 \text{ Ma})$ in the Middle Ordovician Estancia San Isidro Formation is likely derived from the magmatic arc source that supplied K-bentonites (ca. 470 Ma) to the Precordillera, while a 529 \pm 7 Ma grain from the Estancia San Isidro Formation could have been derived from recycled San Isidro Olistolith (abundant 500–600 Ma grains; Finney et al., 2005). Finney et al. (2005) pointed out that such ages (along with the 600-700 Ma population) are compatible with sources in the adjacent eastern Sierras Pampeanas (Rapela et al., 1998b; Sims et al., 1998; Schwartz & Gromet, 2004), although ca 535 Ma rift-related plutons in the Oklahoma Aulacogen also intersect the Ouachita Embayment, and could therefore be a component in the Precordillera basement according to the Thomas-Astini early Cambrian rifting model (Thomas et al., 2004). Three Archaean-age zircons in the 2.6–2.7 Ga range find duplication in a recently analysed sample from the Lower Cambrian Cerro Totora Formation, which contains a single 2.6 Ga grain (Finney, 2006). Such ages are neither distinctive of Laurentia or Gondwana, though they are a key component of Lower Palaeozoic clastic units from southern Laurentia (Gleason et al., 2002; Thomas et al., 2004). There is striking resemblance between the zircon age spectra of the Middle Ordovician Estancia San Isidro Formation and the Middle Cambrian La Laja Formation (Finney et al., 2005), both of which contain abundant 1200-1700 Ma zircons. The San Isidro Olistolith also contains a small percentage of grains of this age, while the Cerro Totora Formation contains an abundance of ca 1.4 Ga grains (Finney, 2006). These comparisons suggest that local basement rocks were a regional source of *ca* 1.4 Ga zircons in the Precordillera Terrane from the Cambrian onwards.

Although the La Laja and San Isidro Olistolith Middle Cambrian clastic units from the Precordillera platform appear to be largely devoid of Grenvillian-age zircons (0% of 1.0–1.2 Ga; Finney et al., 2005), this age range is well-represented by the Lower Cambrian Cerro Totora Formation (Thomas et al., 2004), and is also the inferred age for most of the Precordillera basement, in addition to comprising >50% of grains dated here from Upper Ordovician units. Finney et al. (2005) and others (e.g. Schwartz & Gromet, 2004) have pointed out that abundant Grenvillian-ages (1.0-1.2 Ga) are neither distinctive of Gondwana nor Laurentia, nor is the 1.4 Ga signature (large numbers of *ca* 1.4 Ga plutons are being dated on the Amazon craton; e.g. Geraldes et al., 2001). In addition, abundant 1.5-1.6 Ga zircon ages in Precordilleran Middle Cambrian clastic units (>33%), plus their potentially recycled variants in the Ordovician clastic units (ca 5%), seem to be distinctly non-Laurentian (Finney et al., 2005). This component cannot be attributed strictly to an external Gondwanan terrane supplying material only in the Ordovician, as these sources were

evidently also supplying the Precordillera passive margin platform during the Cambrian. Nonetheless, the large proportions of detrital zircons with ages compatible with a Laurentian origin could be used to argue that the Thomas-Astini hypothesis, with an origin for the Precordillera terrane in the Ouachita Embayment of North America, is fundamentally correct. Thomas et al. (2004) have provided detrital zircon data that would allow for a shared provenance between early Cambrian rift basins along the eastern edge of the Ouachita Embayment (Birmingham Graben) and the northern end of the Precordillera Terrane. The large numbers of 1.0–1.2 Ga zircons in the Ordovician detrital zircon data set could have been largely derived either from local basement sources (e.g. Sierra de Pie de Palo basement) or possibly their recycled variants in early Cambrian rift/cover assemblages (e.g. Cerro Totora Formation), neither of which were evidently exposed during the time that Middle Cambrian clastic units (Finney et al., 2005) were being deposited on the Precordillera platform.

CONCLUSIONS

A combination of petrographic, U-Pb detrital zircon, and Nd-Pb whole-rock isotopic data for graptolite-bearing Middle and Upper Ordovician siliciclastic facies of the Argentine Precordillera indicate mixed sedimentary sources consisting of recycled Precordillera basement, older platform facies, and a high- μ (U/Pb) Gondwanan terrane(s). Upper Ordovician sandstone samples from the eastern Precordillera yield complex U-Pb detrital zircon age spectra characterized by abundant ca 1.0-1.5 Ga zircons, while a Middle Ordovician sandstone unit is dominated by ca 1400 Ma zircons. These ages are consistent with a major component of local Precordillera basement and its derivatives (i.e. lower Palaeozoic siliciclastic units of the Precordillera sedimentary succession) as the primary source of sediment supplying Precordilleran basins in the Ordovician. Common Pb data for Middle and Upper Ordovician graptolitic shales from the western and eastern Precordillera provide evidence for a high-µ U/Pb (Gondwanan?) source (up to 30%). Despite significant overlap, a regional trend towards greater homogenization and less negative Nd values in the sedimentary system is observed between Middle Ordovician shales ($\varepsilon_{\rm Nd} = -7.3 \pm 0.9$; $T_{\rm DM} = 1.60 \pm 0.12$; n = 14) and Upper Ordovician shales (-5.9 ± 0.7 ; $T_{\rm DM} = 1.46 \pm 0.12$ Ga; n = 12) of the eastern and central basins. The Nd, U-Pb and petrographic data suggest that various sub-basins were being supplied at times by distinct sediment sources, particularly the San Juan (Cerro La Chilca) and San Isidro sub-basins in the Middle Ordovician, and the San Rafael subbasin during the Late Ordovician. Therefore, transient 'along-strike' (north to south) variations in sources, as well as temporal variations, may have existed regionally for the Precordillera Ordovician siliciclastic assemblage. Lack of direct evidence for sources in the Famatina Arc (ca 500– 470 Ma) indicates either (1) a more distant location for the Precordillera during this time, or (2) that local basement sources dominated at all the localities sampled.

These data are compatible with basin evolution models that interpret the disintegration of the Precordillera Cambro-Ordovician platform by flexural extension of an evolving foreland basin along the proto-Andean margin of Gondwana (Astini et al., 1995); however, they also do not rule out other basin evolution models favouring diverse extensional tectonic environments, including (1) continental margin pull-apart basins along an active strike-slip (transcurrent) fault zone, (2) regional extension along an oblique subduction zone, or (3) active rifting. The broad similarities in isotopic composition between the western and eastern basins are generally consistent with the hypothesis for a regionally developed clastic wedge that was supplied by recycled orogenic sources lying dominantly to the east (Astini et al., 1995; Astini, 1998a). However, independent analysis has called into question a genetic link between Ordovician depositional systems of the western basins and the rest of the Precordillera. Eastern sources like the Sierra de Pie de Palo Precambrian basement are most consistent with the isotopic data presented in this study, but with the following caveats: (1) Sierra de Pie de Palo basement is yet to be confirmed as a true extension of the basement upon which the Precordillera platform was deposited, and (2) similar-age basement may have also existed along other parts of the proto-Andean margin of West Gondwana (e.g. Schwartz & Gromet, 2004). Evidence for increasing isotopic homogenization of sediment sources upsection in the eastern and central basins is perhaps surprising given the chaotic nature of Middle and Upper Ordovician siliciclastic sedimentation in the Precordillera, and is interpreted here as being partly a consequence of cannibalistic recycling within the Precordillera Lower Palaeozoic succession. The data presented here appear to

rule out any directly shared heritage of Ordovician siliciclastic successions between the Precordillera and the southern margin of Laurentia, placing severe constraints on the Ordovician rifting models of Keller (1999) and Dalla Salda *et al.* (1992a). The data are, however, consistent with either a foreland basin clastic wedge provenance (Astini *et al.*, 1995), or strike-slip (pull-apart) basin model (Finney, 2006) for the evolution of the Precordillera Ordovician siliciclastic succession.

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SUPPLEMENTARY MATERIAL

The following supplementary material is available for this article online:

Appendix S1. Electronic supplement.

Table S1. Petrographic description of Precor-dillera Ordovician Sandstones.

Table S2. U-Pb detrital zircon geochronology of Precordillera Ordovician sandstones.

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