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Detrital chromian spinels from Upper Ordovician deposits in the Precordillera terrane, Argentina: A mafic crust input

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ABSTRACT

The study of heavy minerals from the Caradocian Pavón Formation (central Argentina) suggests that MORB and continental intraplate flood basalts were among the source rocks for the detrital record. The Pavón Formation was deposited on the disputed exotic Precordillera terrane. Provenance studies on this formation revealed sedimentary rocks characterized by an upper continental crustal component mixed with a mafic source, where the latter could not be described. The detrital chromian spinels provide more information about this component.

The detrital spinels were chemically separated into two groups. Group 1 shows characteristics typical for host rocks related to MORB (Cr# values are between 0.4 and 0.6, Fe^{2+}# range from 0.2 to 0.4, and they have low TiO_2 and low Fe^{3+}# contents). Conversely, Group 2 has Cr# of 0.7, Fe^{2+}# ranging from 0.5 to 0.8, higher Fe^{3+}# and TiO_2 contents up to 4.7%, and they are related to continental flood basalts.

The detrital spinels are chemically and texturally compared to those hosted in probable source rocks. Although the mafic source still remains unknown, the presence of detrital chromian spinels within the Pavón Formation implies the existence of an oceanic crustal component closely related to the Precordillera terrane.

1. Introduction

The origin and evolution of the Precordillera terrane has been debated for years; although there is a general consensus about its allochthonous (or para-autochthonous) character, it has not been proved whether the Precordillera is a crustal block derived from Laurentia (Ramos et al., 1986; Dalla Salda et al., 1992; Cingolani et al., 1992; Dalziel et al., 1994; Astini et al., 1995; Kay et al., 1996; Keller, 1999), or a block located southwards (present coordinates) in West Gondwana during the Lower Palaeozoic and later displaced by strike-slip movements along the Gondwana margin (Baldis et al., 1982; Aceñolaza et al., 2002; Finney et al., 2003a, 2005).

Several lines of research (sedimentology, biostratigraphy, geochronology, palaeomagnetism, isotope geochemistry) support the palaeogeographic proximity of this terrane to Laurentia (Benedetto, 1993; Lehnert and Keller, 1993; Buggisch et al., 1993; Ramos et al., 1998; Thomas et al., 2001; Rapalini and Cingolani, 2004) and allowed the development of different models to explain the transference from Laurentia to Gondwana (Ramos et al., 1986; Dalla Salda et al., 1992; Astini et al., 1995; Thomas and Astini, 1996; Dalziel, 1997; Ramos et al., 1998; Keller, 1999; Buggisch et al., 2000). Although all these models assume a collision between the two continents, they differ primarily in the time and type of collision. However, a Gondwana affinity for the early Palaeozoic was recently provided by U–Pb ages on detrital zircons (Finney et al., 2003a, b, 2004, 2005), focusing the discussion again on the origin of the Precordillera terrane.

The Precordillera *sensu stricto* (see Fig. 1a) was initially defined as a geological Province of western Argentina. Since it was considered as a probable exotic mass, the term changed slightly to "Precordillera terrane" (Ramos et al., 1986). The terrane was later expanded to include other exotic blocks, which share the same characteristics for the lower Palaeozoic as well as a Grenvillian-type basement, and are currently accepted as the continuation of the Precordillera *sensu stricto* (Astini et al., 1995). It was also named the "Cuyania composite terrane" (Ramos et al., 1996) including the Western Pampeanas Ranges and the San Rafael and Las Matras blocks (see Fig. 1a). The existence of the Cuyania or Precordillera terrane was argued by Dalla Salda et al. (1992), who proposed the alternative concept of the Occidentalia terrane, which includes the Precordillera terrane and all the surrounding areas with a Grenvillian-age basement (from Arequipa to Northern

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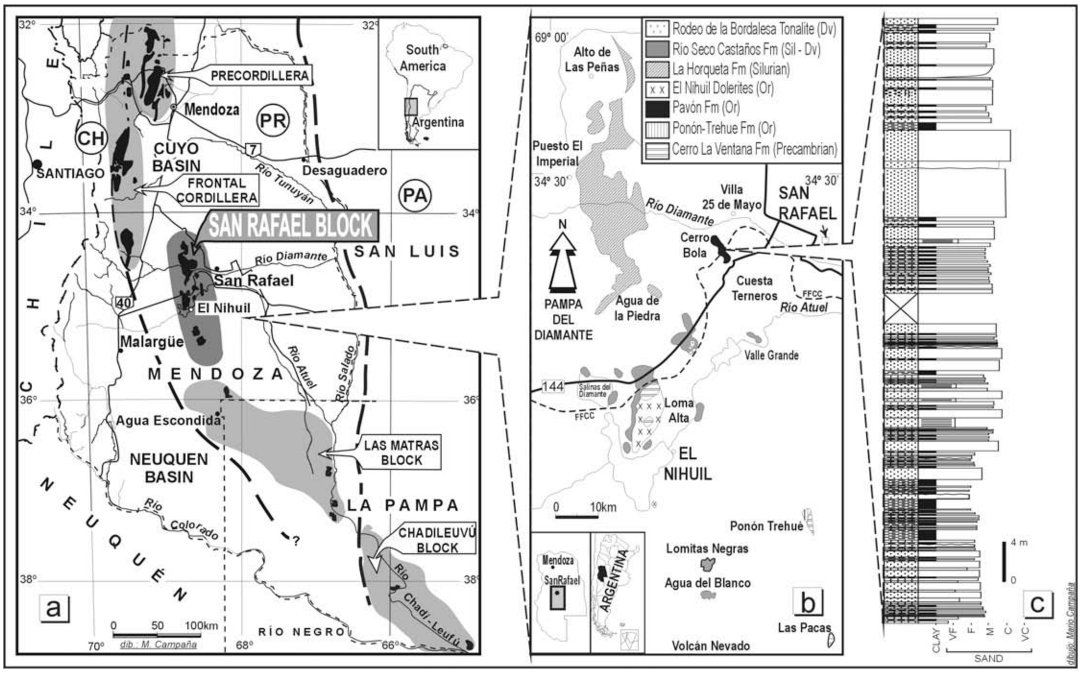

Fig. 1. (a) Location of the Precordillera *s.s.* and San Rafael block, central Argentina. PR = Precordillera (Cuyania) Terrane; PA = Pampia Terrane; CH = Chilenia Terrane. (b) Geological sketch map of the San Rafael block; see outcrops of the Pavón Formation in the central part. (c) Simplified stratigraphic section of the Pavón Formation (integrated column) showing the coarsening and thickening upward trend (modified from Manassero et al., 1999); VF: very fine; F: fine; M: medium; C: coarse; VC: very coarse.

Patagonia). The use of the term "Precordillera terrane" in the sense of Astini et al. (1995) is preferred throughout this study.

Notwithstanding the relevance of understanding the evolution of the Western Gondwana margin, provenance studies of its sedimentary record are scarce. One example is that of Cingolani et al. (2003), who studied the Upper Ordovician Pavón Formation clastic sequence. This unit is part of the San Rafael block, in central western Mendoza Province, Argentina (Fig. 1b), which represents the southward continuation of the Precordillera *sensu stricto*. These authors stated that the Pavón Formation had a complex provenance history. QFL data indicate an upper continental crust composition source, but relative high abundances of V, Cr, Ni, Ti and Sc suggest a mafic input. However, the techniques used did not allow identification of the nature of that mafic source, since it could be derived either from a MORB (mid-ocean ridge basalt) ophiolite, island arc or from ultramafic volcanic rocks such as kimberlites or komatiites. In order to decipher the provenance and constrain the tectonic setting and continental evolution, the heavy mineral assemblage was studied.

Heavy minerals are a reliable tool in determining the nature of sedimentary source areas, especially when other techniques (geochemistry, petrography and Nd isotopes) show source mixing, but the origin of these sources are indecipherable. They are particularly useful in studies of sedimentation related to tectonic uplift, as the evolution and unroofing episodes of orogenic belts are reflected in adjacent basin sediments. Analysis of heavy minerals in foreland basin sequences may thus prove valuable in constraining the structural histories of both the basin and the source areas (Mange and Maurer, 1992) and give important clues to the composition of the sources.

Detrital heavy mineral species from the Pavón Formation were identified using a binocular microscope and energy dispersive system (EDS). Spinel chemistry was determined by electron microprobe analysis. Other associated mineral species, e.g. zircon, rutile and apatite have been described previously (Abre et al., 2003) and are not discussed in detail here, as they do not contribute to the characterization of the mafic source. The discovery of detrital chromian spinel (Abre et al., 2005) provides a new insight into the palaeogeographic evolution of the Precordillera terrane, since the spinels represent a remnant of a pre-Caradoc mafic source(s) in Ordovician sedimentary rocks of the southern limb of the Precordillera terrane.

The objective of the present work is to describe the composition of the chromian spinels in the heavy mineral assemblage, in order to determine the tectonic setting of their initial host rocks. Different areas surrounding the Precordillera terrane are tested as probable sources in relation to the models that attempt to explain the geotectonic evolution of this terrane.

2. Geological background

The Pavón Formation crops out in the central region of the San Rafael block, Mendoza province, central Argentina (Fig. 1a). It is bounded by the Cuyo and Neuquén oil basins to the north and southwest, respectively, by the Andean Cordillera to the west and is overlain by modern cover towards the east. The San Rafael block comprises Precambrian and lower-middle Palaeozoic rocks (Fig. 1b), which are clearly separated from upper Palaeozoic strata by a regional unconformity. Permian–Triassic magmatism and Cenozoic volcanism are present (Dessanti, 1956; Polanski, 1966; González Díaz, 1972). The San Rafael block is a key area in the evolution of the proto-Andean margin of southwestern Gondwana, as it is considered a southward continuation of the proposed Laurentian-derived Precordillera terrane.

As summarized by Cingolani et al. (2003) and references therein, the Pavón Formation is a massive, thick (700 m) clastic series composed of arenites, wackes, silicate–siltstones and claystones (Fig. 1c). The illite crystallinity index suggests very low-grade metamorphic conditions (Manassero et al., 1999). A rich graptolite fauna found in several levels provides an early Caradoc age (*Climacograptus bicornis* biozone; Cuerda et al., 1998). The sequence was deposited as sandy marine turbidites (Manassero et al., 1999). Sandstones have 15–30% matrix, poor to moderate sorting and fine- to very fine-grain sizes. They are composed of quartz, K-feldspar, plagioclase, sedimentary and metamorphic lithoclasts, biotite, muscovite, zircon, apatite, magnetite and hematite (Cingolani et al., 2003). Petrographic provenance analysis suggests a recycled orogen and a continental block as the main source areas (Manassero et al., 1999). Geochemical data demonstrated that the Pavón Formation displays detrital components of an upper continental crust composition mixed with a less fractionated component (Cingolani et al., 2003). Th/Sc and Zr/Sc ratios reflect significant reworking with most input from upper crustal sources. However, Cr, Ni, V, Ti and Sc contents are enriched relative to average continental crust composition. The general character of the less fractionated source was interpreted as a mafic to ultramafic component (Cingolani et al., 2003). Nd model ages of Pavón sandstones scatter around 1.4 Ga, with an affinity to Grenvillian-age crust, and they differ significantly from the general Gondwana-like signature in northwestern Argentina (Cingolani et al., 2003).

The Pavón Formation clastic sequence was deposited in a foreland basin at the latitude of 25.7 ± 2.9° S (Rapalini and Cingolani, 2004). This basin was related to the accretion of the Precordillera terrane located west of Gondwana; this accretion caused uplift by thrusting of the Grenvillian-age crust to the east at ca. 460 Ma (Ramos et al., 1996; Cingolani et al., 2003).

3. Analytical techniques

Five wacke samples were crushed and sieved in at least three fractions. The less than 100 μm fraction was selected in order to avoid confusing results because of the hydrodynamic fractionation shown by samples with different grain sizes (Morton and Hallsworth, 1994). From the less than 100 μm population a pre-concentrate of the heaviest fraction was obtained by settling in a back current of water active in a glass tube. This pre-concentrate was treated with bromoform ($\delta = 2.89$) to obtain the complete heavy minerals fraction. The heavy minerals separation laboratory of the Centro de Investigaciones Geológicas (La Plata University, Argentina) was used for this work.

The heavy mineral fraction was embedded randomly into epoxy resin, polished and carbon coated. The identification and characterization (shape, size, fractures and inclusions) of the heavy minerals were done using a binocular microscope, scanning and backscattered electron microscope using energy dispersive spectrometry (SEM–BSE–EDS). A JEOL JSM-5600 with a tungsten filament was used and EDS analyses were undertaken using a Noran X-ray detector and Noran Vantage software. The SEM–BSE–EDS system was set at 15 keV, a working distance of 20 mm and a live time of 60 s per spot.

Quantitative analyses of the spinels were carried out with a Cameca 355 electron microprobe equipped with an Oxford link integrated WDS/EDS set at a voltage of 15 keV, and with a JEOL 733 with WDS/EDS set at a voltage of 15 keV. Beam current diameter in both microprobes was between 8 and 10 μm; ZAF corrections were effected under standard procedures. Chromite standard on MAC certified standard no. 2590 was used for analysis. The Centralized Analytical Facility (SPECTRAU), University of Johannesburg, South Africa, provided all the above mentioned analytical equipment.

As only total iron is measured with the electron microprobe, the stoichiometric compositions of the spinels were calculated using a Visual Basic macro in Microsoft Excel based on the stoichiometric formula of spinels, in order to discriminate Fe^{2+} and Fe^{3+}. Accuracy and precision of such calculations are imperfect (Wood and Virgo, 1989). However, these errors become significant for calculating oxygen fugacity, but are precise and accurate enough to obtain Fe^{3+} and Fe^{2+} contents (Wood and Virgo, 1989). Each grain was measured several times (two to five spots) depending on grain size and then an average composition was computed (Table 1), as differences due to fractionation could not be observed in any one grain.

4. Results

The detrital heavy mineral assemblage is predominantly composed of zircon, spinel and rutile in order of abundance; these are widely known as ultrastable phases since they are mechanically and chemically resistant to sedimentary degradation (Morton and Hallsworth, 1999). Less abundant are apatite and sphene (Abre et al., 2003). Only a few heavy minerals could be used for provenance studies using microprobe analytical techniques. In this paper, the focus is on spinels as indicators of a mafic to ultramafic source, which could give some important insights on the palaeotectonic setting of Ordovician deposits from the Precordillera terrane.

Spinel grains contained in sedimentary rocks can provide important information regarding source areas closely related to the depositional site (Arai, 1992; Oberhänsli et al., 1999; Asiedu et al., 2000; Garzanti et al. 2000, 2002; Zhu et al., 2004). The main tool to decipher the nature of the source is geochemical analysis of individual grains, as melting and crystallization processes depend on tectonic setting, and can be recorded in the chemistry of a single grain (Dick and Bullen, 1984; Kamenetsky et al., 2001; Barnes and Roeder, 2001). In this study, mafic to ultramafic rocks are known to be the source of detrital record for the Pavón Formation and the spinels will give some important clues regarding the nature of this source.

The spinels occur in fine-grained, poor- to moderate-sorted wackes of the Pavón Formation. The Cr content of this unit varies between 65 and 292 ppm and has an average of 139 ppm (Cingolani et al., 2003), which represents an enrichment compared with the average Cr content of wackes and shales (Cr = 67 and 88 ppm, respectively according to Taylor and McLennan, 1985). The layers sampled for this study show elevated Cr concentrations of 152 ppm on average.

Spinel is a mineralogical group of oxides with a general formula AB_2O_4, were A = Fe^{2+}, Mg, Mn, Zn, Ni, Ca and B = Fe^{3+}, Al, Cr, Ti, V, Si. It is subdivided according to whether the trivalent ion is Al (spinel series), Fe^{3+} (magnetite series) or Cr (chromite series). The chromite series is known as chromian spinel or brown spinel, and consists of two minerals: magnesiochromite and chromite. Pure end-members of the spinel group are rare in nature. Chromites have a wide range in composition because of the substitutions of Mg for Fe^{2+} and of Al and Fe^{3+} for Cr. Based on their chemical composition the term chromian spinel is used here for the spinels in the Pavón Formation. 'Spinel' is used to name the entire group (in a broad sense) and spinel *sensu stricto* (*s.s.*) to refer to the Al-rich series.

The chemical composition of the separated chromian spinels varies markedly: the Cr# = Cr/(Cr + Al) atomic ratios range from 0.40 to 0.77 and the Mg# = Mg/(Mg + Fe^{2+}) atomic ratios range from 0.2 to 0.8 (Table 1). Cr content has an average of 41.1%, the Fe^{2+}/Fe^{3+} ratio ranges between 1.7 and 5.0. Spinels with highest Cr# have also high TiO_2 (up to 4.7%) and total Fe contents, while Al_2O_3 and MgO are low (Table 1).

Based on chemistry, the data could be separated into two groups. Group 1 involves 60% of the grains (plotted as crosses in Figs. 3–7), has a narrow range in Cr# (0.47–0.58) but an expanded range in Mg# (0.50–0.80); they have lower TiO_2 (less than 0.60%) and Fe^{3+}# ratio (Fe^{3+}# = Fe^{3+}/(Cr+Al+Fe^{3+})) compared with Group

Table 1
Chemical composition of detrital chromian spinels from the Pavón Formation.

Sample	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO_2	MnO	MgO	CaO	V_2O_5	NiO	ZnO	Total	Fe_2O_3	FeO
Group 1														
2	0.13	0.51	26.81	36.19	17.61	0.17	15.69	0.04	0.16	0.25	0.31	97.86	6.70	11.58
23	0.01	0.39	24.97	38.41	22.17	0.24	11.88	0.01	0.09	0.27	0.28	98.72	5.63	17.11
c1	0.06	0.54	25.31	38.75	19.99	0.05	13.07	0.00	0.23	0.00	0.30	98.29	4.61	15.84
c2	0.02	0.35	27.49	37.47	15.70	0.00	16.61	0.01	0.16	0.02	0.11	97.93	5.63	10.63
48	0.09	0.37	23.79	41.47	17.73	0.33	15.17	0.02	0.19	0.28	0.00	99.45	5.97	12.36
c3	0.07	0.44	27.83	36.38	14.66	0.05	16.93	0.02	0.17	0.31	0.43	97.29	5.73	9.51
37	0.17	0.39	27.34	40.38	15.47	0.22	16.85	0.06	0.07	0.32	0.04	101.30	4.92	11.04
45	0.28	0.60	22.47	46.82	14.87	0.51	16.08	0.17	0.18	0.46	0.03	102.45	3.66	11.58
a	0.16	0.40	27.23	38.85	16.56	0.18	16.85	0.01	0.00	0.42	0.12	100.77	6.42	10.78
e	0.22	0.22	23.16	39.88	21.17	0.51	13.65	0.12	0.17	0.29	0.17	99.56	7.73	14.22
c	0.15	0.41	22.78	37.94	23.44	0.20	13.45	0.17	0.34	0.44	0.12	99.44	9.72	14.69
b	0.19	0.43	31.12	33.33	17.05	0.35	16.46	0.05	0.53	0.29	0.14	99.93	5.95	11.69
s	0.44	0.50	24.12	39.60	24.11	0.43	11.01	0.13	0.07	0.20	0.13	100.71	5.15	19.48
i	0.12	0.41	23.07	43.74	17.14	0.14	15.09	0.10	0.00	0.55	0.00	100.35	5.10	12.55
m	0.17	0.51	26.30	38.65	18.42	0.43	15.57	0.08	0.00	0.07	0.25	100.45	6.57	12.51
q	0.29	0.57	23.56	42.30	18.85	0.47	15.16	0.09	0.00	0.00	0.00	101.26	6.05	13.40
n	0.18	0.24	31.77	31.04	21.34	0.10	14.06	0.04	0.01	0.35	0.80	99.93	7.17	14.89
r	0.18	0.48	23.11	45.30	12.36	0.39	18.03	0.12	0.00	0.57	0.06	100.58	4.93	7.92
u	0.08	0.40	23.76	43.26	14.14	0.58	16.82	0.09	0.07	0.76	0.06	100.00	5.55	9.15
t	0.13	0.51	27.08	38.97	18.57	0.50	14.82	0.05	0.11	0.27	0.07	101.07	5.26	13.84
ae	0.23	0.35	23.96	43.19	15.01	0.59	16.38	0.00	0.00	0.07	0.11	99.88	4.82	10.67
af	0.01	0.58	24.14	36.91	22.99	0.38	13.73	0.00	0.00	0.47	0.08	99.29	9.52	14.42
Average	0.15	0.43	25.51	39.49	18.15	0.31	15.15	0.06	0.12	0.30	0.16	99.84	6.04	12.72
Group 2														
23-6	0.05	3.10	11.77	45.06	35.22	0.41	4.29	0.18	0.18	0.27	0.45	100.94	6.51	29.36
38	0.16	3.99	10.39	40.53	38.18	0.29	7.37	0.10	0.27	0.60	0.01	101.88	13.46	26.07
40	0.16	2.26	11.97	45.66	27.68	0.13	10.22	0.02	0.11	0.38	0.13	98.71	8.92	19.65
14	0.02	3.43	11.15	40.37	32.54	0.18	9.90	0.00	0.21	0.05	0.00	97.85	12.71	21.10
ad	0.01	2.73	12.71	41.84	32.94	0.19	11.12	0.06	0.00	0.00	0.07	101.67	14.39	19.99
f	0.13	2.73	11.76	44.42	32.10	0.50	9.26	0.12	0.35	0.36	0.24	101.97	11.23	22.00
w	0.06	3.94	10.40	42.11	35.18	0.29	9.15	0.14	0.00	0.00	0.22	101.49	13.11	23.38
d	0.09	3.01	10.21	40.75	38.83	0.88	5.64	0.03	0.00	0.20	0.17	99.81	13.39	26.78
g	0.11	4.70	11.44	40.78	32.89	0.35	10.31	0.11	0.33	0.45	0.00	101.45	11.84	22.23
h	0.16	2.15	8.88	45.36	36.76	0.43	5.49	0.13	0.21	0.00	0.37	99.94	11.43	26.48
p	0.15	1.66	13.63	46.33	31.30	0.32	7.06	0.10	0.02	0.49	0.45	101.51	7.67	24.40
o	0.17	2.27	12.35	45.43	30.11	0.24	11.01	0.09	0.11	0.00	0.17	101.95	11.50	19.76
v	0.18	3.03	11.22	44.13	33.05	0.69	8.37	0.12	0.00	0.39	0.79	101.97	11.30	22.88
aa	0.16	2.49	13.52	45.46	27.87	0.37	9.73	0.11	0.16	0.41	0.72	101.00	8.01	20.67
ac	0.01	3.02	12.69	42.60	32.25	0.36	8.28	0.09	0.51	0.00	0.26	100.07	9.59	23.62
Average	0.11	2.97	11.61	43.39	33.13	0.37	8.48	0.09	0.16	0.24	0.27	100.81	11.00	23.23

Sample	Si	Ti	Al	Cr	Fe^{3+}	Fe^{2+}	Mn	Mg	Ca	V	Ni	Zn
Group 1												
2	0.004	0.011	0.952	0.862	0.152	0.292	0.004	0.705	0.001	0.004	0.006	0.007
23	0.000	0.009	0.910	0.939	0.131	0.442	0.006	0.548	0.000	0.002	0.007	0.006
c1	0.002	0.012	0.917	0.942	0.107	0.407	0.001	0.599	0.000	0.006	0.000	0.007
c2	0.000	0.008	0.968	0.885	0.127	0.266	0.000	0.740	0.000	0.004	0.000	0.002
48	0.003	0.008	0.847	0.990	0.136	0.312	0.008	0.683	0.000	0.005	0.007	0.000
c3	0.002	0.010	0.982	0.861	0.129	0.238	0.001	0.755	0.001	0.004	0.007	0.010
37	0.005	0.009	0.936	0.928	0.108	0.268	0.005	0.730	0.002	0.002	0.007	0.001
45	0.008	0.013	0.781	1.091	0.081	0.285	0.013	0.707	0.005	0.004	0.011	0.001
a	0.005	0.009	0.936	0.896	0.141	0.263	0.004	0.733	0.000	0.000	0.010	0.003
e	0.007	0.005	0.833	0.962	0.177	0.363	0.013	0.621	0.004	0.004	0.007	0.004
c	0.005	0.009	0.822	0.918	0.224	0.376	0.005	0.614	0.006	0.008	0.011	0.003
b	0.006	0.009	1.064	0.764	0.130	0.284	0.008	0.711	0.002	0.012	0.007	0.003
s	0.013	0.011	0.871	0.959	0.119	0.499	0.011	0.503	0.004	0.002	0.005	0.003
i	0.004	0.009	0.818	1.041	0.116	0.316	0.004	0.677	0.003	0.000	0.013	0.000
m	0.005	0.011	0.917	0.904	0.146	0.309	0.011	0.687	0.003	0.000	0.002	0.005
q	0.008	0.013	0.827	0.996	0.135	0.334	0.012	0.673	0.003	0.000	0.000	0.000
n	0.005	0.005	1.100	0.721	0.158	0.366	0.002	0.616	0.001	0.000	0.008	0.017
r	0.005	0.011	0.803	1.056	0.109	0.195	0.010	0.792	0.004	0.000	0.014	0.001
u	0.002	0.009	0.834	1.018	0.124	0.228	0.015	0.747	0.003	0.002	0.018	0.001
t	0.004	0.011	0.942	0.909	0.117	0.341	0.012	0.652	0.002	0.003	0.006	0.002
ae	0.007	0.008	0.843	1.019	0.108	0.266	0.015	0.729	0.000	0.000	0.002	0.002
af	0.000	0.013	0.866	0.889	0.218	0.367	0.010	0.623	0.000	0.000	0.012	0.002
Average	0.005	0.010	0.898	0.934	0.136	0.319	0.008	0.675	0.002	0.003	0.007	0.004
Group 2												
23-6	0.002	0.079	0.468	1.202	0.165	0.828	0.012	0.216	0.006	0.005	0.007	0.011
38	0.005	0.098	0.402	1.052	0.332	0.716	0.008	0.361	0.004	0.007	0.016	0.000
40	0.005	0.056	0.465	1.189	0.221	0.541	0.004	0.502	0.001	0.003	0.010	0.003
14	0.001	0.086	0.438	1.064	0.319	0.588	0.005	0.492	0.000	0.006	0.001	0.000

Table 1 (*continued*)

Sample	Si	Ti	Al	Cr	Fe^{3+}	Fe^{2+}	Mn	Mg	Ca	V	Ni	Zn
ad	0.000	0.065	0.475	1.050	0.344	0.531	0.005	0.526	0.002	0.000	0.000	0.002
f	0.004	0.066	0.447	1.132	0.272	0.593	0.014	0.445	0.004	0.009	0.009	0.006
w	0.002	0.096	0.399	1.083	0.321	0.636	0.008	0.444	0.005	0.000	0.000	0.005
d	0.003	0.077	0.408	1.092	0.341	0.759	0.025	0.285	0.001	0.000	0.005	0.004
g	0.003	0.114	0.434	1.037	0.287	0.598	0.009	0.494	0.004	0.009	0.012	0.000
h	0.005	0.055	0.357	1.223	0.293	0.755	0.012	0.279	0.005	0.006	0.000	0.009
p	0.005	0.041	0.524	1.196	0.188	0.666	0.009	0.344	0.003	0.001	0.013	0.011
o	0.005	0.054	0.462	1.141	0.275	0.525	0.006	0.521	0.003	0.003	0.000	0.004
v	0.006	0.074	0.430	1.134	0.276	0.622	0.019	0.406	0.004	0.000	0.010	0.019
aa	0.005	0.060	0.513	1.158	0.194	0.557	0.010	0.467	0.004	0.004	0.011	0.017
ac	0.000	0.075	0.492	1.108	0.237	0.650	0.010	0.406	0.003	0.013	0.000	0.006
Average	0.003	0.073	0.448	1.124	0.271	0.638	0.010	0.412	0.003	0.004	0.006	0.007

Sample	Cr#	Mg#	Fe^{2+}#	Fe^{3+}#	Fe^{2+}/Fe^{3+}
Group 1					
2	0.48	0.71	0.29	0.08	1.92
23	0.51	0.55	0.45	0.07	3.38
c1	0.51	0.60	0.40	0.05	3.82
c2	0.48	0.74	0.26	0.06	2.10
48	0.54	0.69	0.31	0.07	2.30
c3	0.47	0.76	0.24	0.07	1.84
37	0.50	0.73	0.27	0.05	2.49
45	0.58	0.71	0.29	0.04	3.51
a	0.49	0.74	0.26	0.07	1.87
e	0.54	0.63	0.37	0.09	2.05
c	0.53	0.62	0.38	0.11	1.68
b	0.42	0.71	0.29	0.07	2.18
s	0.52	0.50	0.50	0.06	4.20
i	0.56	0.68	0.32	0.06	2.73
m	0.50	0.69	0.31	0.07	2.11
q	0.55	0.67	0.33	0.07	2.46
n	0.40	0.63	0.37	0.08	2.31
r	0.57	0.80	0.20	0.06	1.79
u	0.55	0.77	0.23	0.06	1.83
t	0.49	0.66	0.34	0.06	2.92
ae	0.55	0.73	0.27	0.05	2.46
af	0.51	0.63	0.37	0.11	1.68
Average	0.51	0.68	0.32	0.07	2.44
Group 2					
23-6	0.72	0.21	0.79	0.09	5.01
38	0.72	0.34	0.66	0.19	2.15
40	0.72	0.48	0.52	0.12	2.45
14	0.71	0.46	0.54	0.18	1.84
ad	0.69	0.50	0.50	0.18	1.54
f	0.72	0.43	0.57	0.15	2.18
w	0.73	0.41	0.59	0.18	1.98
d	0.73	0.27	0.73	0.19	2.22
g	0.71	0.45	0.55	0.16	2.09
h	0.77	0.27	0.73	0.16	2.57
p	0.70	0.34	0.66	0.10	3.54
o	0.71	0.50	0.50	0.15	1.91
v	0.73	0.39	0.61	0.15	2.25
aa	0.69	0.46	0.54	0.10	2.87
ac	0.69	0.38	0.62	0.13	2.74
Average	0.72	0.39	0.61	0.15	2.49

Note: Oxides in percentages. Number of ions based on four oxygen atoms.

2. MnO, V_2O_5, NiO and ZnO contents are very low (see Table 1). Both groups of chromian spinels were found together within the same sampled layers.

Group 2 comprises 40% of the spinel grains with a distinctive chemical composition (represented as squares in Figs. 3–7); they show very high TiO_2 (between 1.7% and 4.7%, average = 2.97%) and Fe^{2+} contents (average 23.2%), and also display the highest Cr# (average 0.72) and the lowest Mg# (average 0.39). MnO, V_2O_5, NiO and ZnO contents are also very low (see Table 1).

Morphologically the two groups are indistinguishable, since SEM and BSE microphotographs (Figs. 2a and b) show sizes ranging from 40 to 110 μm with an average of 60 μm for both, and the proportion of subhedral, anhedral and euhedral grains are also equal in both groups. They do not show any visible zonation, intergrowth or inclusions. Under the binocular microscope, high- and low-TiO_2 chromites are black.

5. Spinel provenance

Detrital chromian spinel is an abundant and important heavy mineral in sedimentary rocks. It is chemically and mechanically stable and is often the only remnant of tectonic slabs of oceanic crust involved in collision zones (Pober and Faupl, 1988). Chromite is the only igneous mineral that is commonly preserved in metamorphosed serpentinite (Proenza et al., 2004; Ahmed et al.,

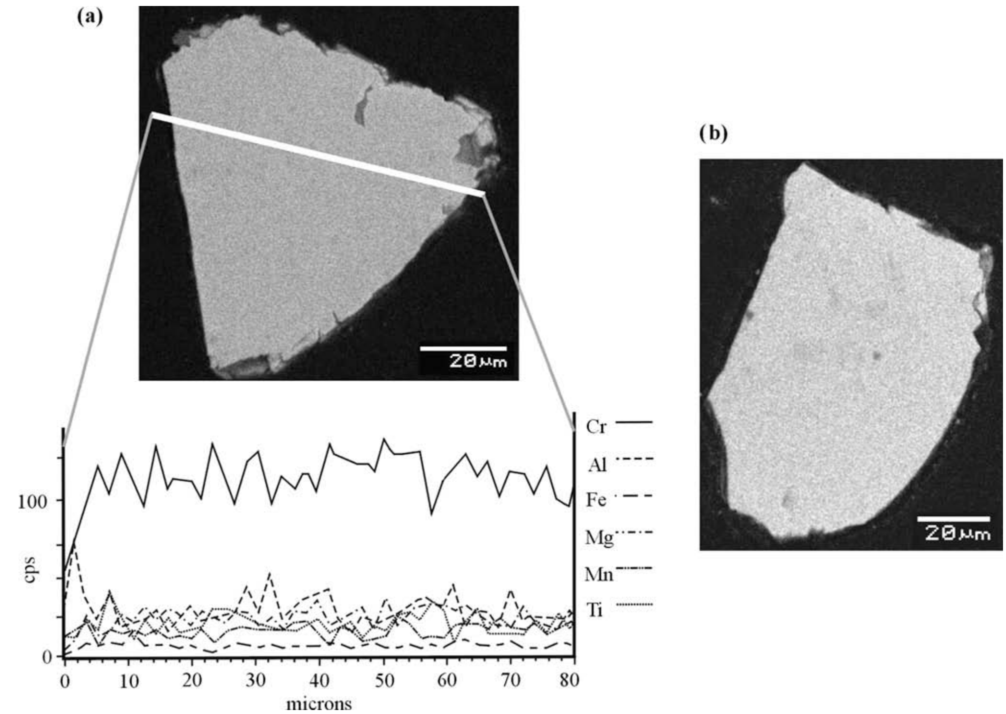

Fig. 2. (a) High TiO_2 chromian spinel from Group 2 under SEM and its microprobe profile showing no chemical zoning. (b) Detrital spinels of Group 1 under SEM, which do not show any chemical zoning either. Bar length is 20 μm; cps: counts per second.

2005). Chromian spinel is an important petrogenetic indicator in mafic and ultramafic rocks because it contains several cations whose atomic ratios vary according to physico-chemical conditions of the parent magma such as composition, cooling rate, crystallization temperature and f_{O_2} (Irvine, 1965, 1967; Evans and Frost, 1975; Dick and Bullen, 1984; Sack and Ghiorso, 1991; Arai, 1992). Because the degree of magma melting determines the chemistry of chromites, and melting conditions depend on geotectonic setting, chromites are widely used in classifying mantle-derived peridotites according to their origin and tectonic setting (Dick and Bullen, 1984; Kamenetsky et al., 2001). Detrital chromian spinel grains are also used in provenance studies of the sedimentary record (Pober and Faupl, 1988; Arai, 1992; Oberhänsli et al., 1999; Asiedu et al., 2000; Garzanti et al., 2000, 2002; Zhu et al., 2004).

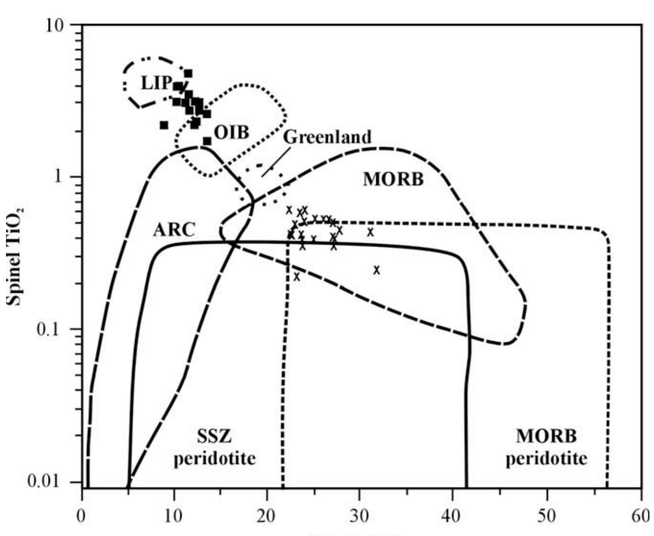

Fig. 3. Spinel TiO_2 vs. Spinel Al_2O_3 after Kamenetsky et al. (2001). Group 1 is represented by crosses and plots as MORB while Group 2 is represented by squares and plots in the LIP and OIB fields and between them. SSZ: supra-subduction zone; OIB: ocean island basalts; LIP: large igneous provinces; MORB: mid-ocean ridge basalt.

Chromian spinel might exhibit chemical zoning due to changes in the composition of both melt and solid phases during crystallization. Assuming that the well-developed crystal boundaries of subhedral grains may preserve the original chemical zonation in detrital grains, microprobe profiles were constructed in order to determine any type of variation. No compositional variations were determined as there is no difference between core and rim, neither intergrowths nor exsolution of other mineral species. These can be seen in Fig. 2a and b where high- and low-TiO_2 spinels (Group 2 and Group 1, respectively) are shown. A microprobe profile on a spinel from Group 2 is shown in order to demonstrate that there is no chemical zoning (Fig. 2a). However, no spinels from Group 1 show any chemical zoning either. This homogeneous pattern indicates that there was no sub-solidus re-equilibration between spinels and other minerals (Scowen et al., 1991).

Kamenetsky et al. (2001) proposed a differentiation between volcanic and so-called "mantle" spinels based on chemical parameters. Mantle spinels have TiO_2 less than 0.2% and Fe^{2+}/Fe^{3+} more than 2 while those of volcanic origin have higher TiO_2 contents and Fe^{2+}/Fe^{3+} less than 2. TiO_2 contents of Group 1 scatter around 0.4% while Group 2 is well above the 0.2% limit (Table 1). Based on only such a value (Zhu et al., 2004), a volcanic origin is preferable for the whole dataset.

Tri- and tetravalent cations in spinel experience almost no variation due to re-equilibration after entrapment because of their low diffusivity in minerals (like olivine); thus they are useful to discriminate mantle source of the host rocks of the spinels (Kamenetsky et al., 2001). For example, spinel Al_2O_3 and TiO_2 concentrations depend on the parental melt composition, and therefore, their relationship allows the discrimination between

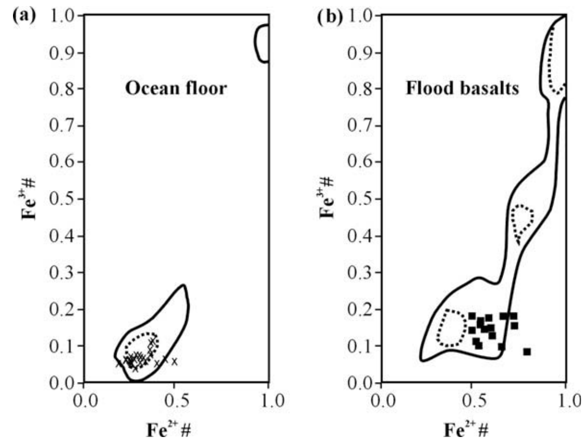

Fig. 4. Fe^{3+}#–Fe^{2+}# relationships based on Barnes and Roeder (2001). The continuous line represents the 90th percentile while the dotted line encloses the 50th percentile. (a) Spinels from Group 1 (crosses) and ocean floor basalts fields for comparison. (b) Spinels from Group 2 (squares) and flood basalts fields for comparison.

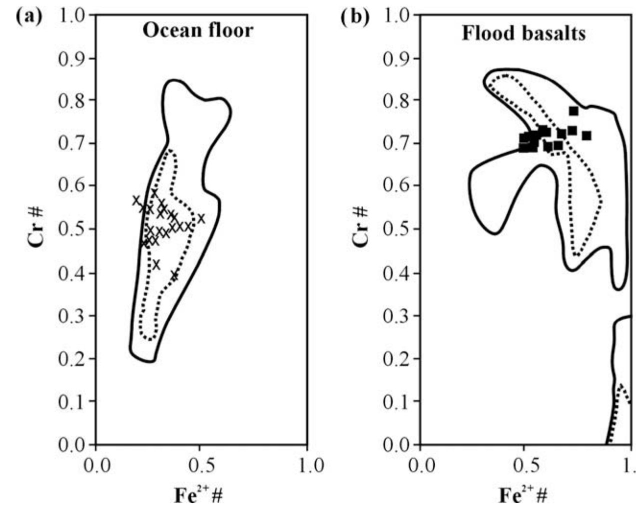

Fig. 6. Cr#–Fe^{2+}# from Barnes and Roeder (2001). References are as in Figs. 3 and 4. (a) Group 1 is clearly ocean-floor related while Group 2 plots as flood basalts (b).

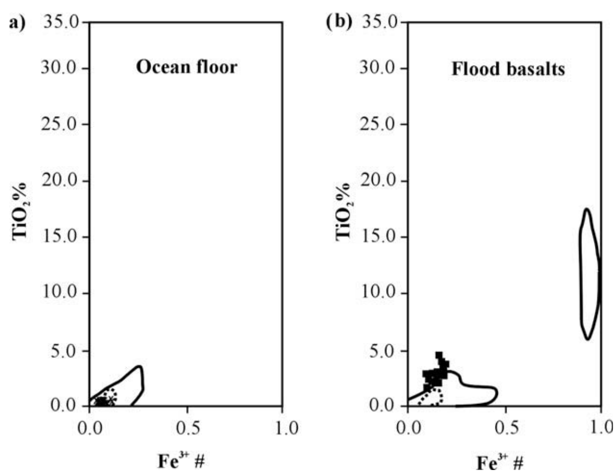

Fig. 5. TiO_2%–Fe^{3+}# diagram from Barnes and Roeder (2001). Sample references are as in Fig. 3 and field references as in previous figure. (a) Spinels from Group 1 plot as ocean-floor related. (b) Spinels from Group 2 plot as continental flood basalts.

different tectonic settings (Kamenetsky et al., 2001). In Fig. 3, Group 1 plots entirely as MORB-related and an arc environment can be discounted. Group 2 displays a continuous array from LIP (large igneous provinces) to OIB (oceanic island basalt) fields.

Chromian spinels from the Pavón Formation have the same composition as the 'tholeiitic basalts and boninites' group from Barnes and Roeder (2001). They are in particular especially comparable to MORB (Group 1) and to continental flood basalts (Group 2; equivalent to LIP in the sense of Kamenetsky et al., 2001), while they differ significantly from ophiolitic basalts, boninites, ocean islands, Hawaiian lava lakes and island arcs. In the Fe^{3+}#–Fe^{2+}# diagram (Fig. 4) spinels from Group 1 plot mainly in the ocean floor basalts field within the 50th percentile line (Fig. 4a), while Group 2 plots in the flood basalts field and within the 90th percentile (Fig. 4b). In the TiO_2–Fe^{3+}# diagram (Fig. 5), Group 1 plots in the ocean floor basalts field again and within the 50th percentile (Fig. 5a); Group 2 plots slightly above the 50th percentile line of the continental flood basalts field, due to their higher Ti content (Fig. 5b). In the Cr–Fe^{2+}# diagram (Fig. 6), spinels from Group 1 plot in the ocean floor field, within the 50th percentile line (Fig. 6a); Group 2 plots in the continental flood basalts field, within both, 50th and 90th percentiles (Fig. 6b). In the Fe^{3+}–Cr–Al triangular diagram (Fig. 7), Group 1 plots within the 90th percentile of the ocean floor field (Fig. 7a) whereas Group 2 plots within the 90th percentile of the flood basalts field (Fig. 7b). However, in all these diagrams Group 1 has a close similarity to basalt xenoliths, but this is not important in the case of provenance analysis, due to their scarcity and low probability of being an important source. Furthermore, spinels from Group 2 correlate with continental flood basalts and are similar to continental mafic intrusions; this is because the dataset for this latter category includes data from some subvolcanic intrusions in flood basalt provinces (Barnes and Roeder, 2001).

6. Source rocks

Previous provenance studies (Cingolani et al., 2003) have shown that the Pavón Formation is of upper continental crust composition mixed with a less fractionated component. The upper continental crustal component is represented by recycled sedimentary rocks and metamorphic fragments, as well as by the product of erosion of igneous rocks (for example, as determined by the analyses of cathodoluminescence images on zircons; Abre et al., 2003). The mafic or ultramafic element is represented by detrital spinels, and is responsible for the less fractionated component in the geochemistry and probably in the Nd-isotope geochemistry (Cingolani et al., 2003).

The detrital chromian spinels of the Pavón Formation were formed within mid-ocean ridge basalts (Group 1) and continental flood basalts (Group 2). The location of the source rocks of these detrital spinels is important regarding the tectonic history and the debated origin of the Precordillera terrane. Possible source areas of mafic to ultramafic rocks that are older than Caradoc from the Precordillera and adjacent areas are shown in Fig. 8 (terrane boundaries are based on Ramos et al. (2000) and Porcher et al. (2004) among others):

(i) In the Western Precordillera ('a' in Fig. 8), a series of discontinuous outcrops of mafic and ultramafic rocks were first assigned to a 'Famatinian ophiolite' sequence (Haller and Ramos, 1984) and interpreted as the suture between the Chilenia and Precordillera terranes (Ramos et al., 1986). However, detailed studies carried out by Davis et al. (1999) show the presence of a number of ophiolite-like units with ages ranging from middle Proterozoic to early Palaeozoic and juxtaposed in the Early to Middle Devonian. Despite

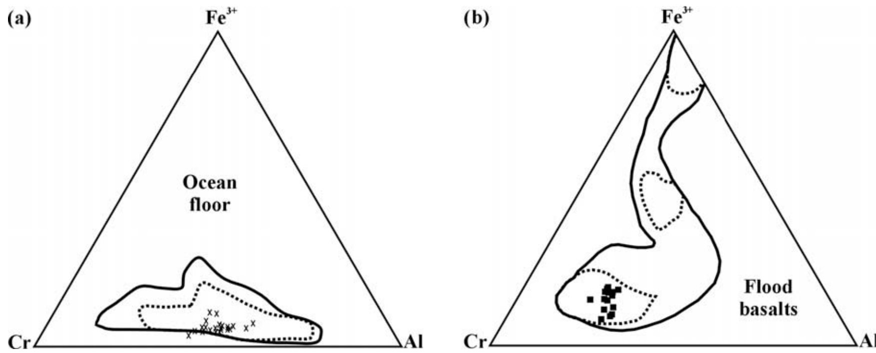

Fig. 7. Fe^{3+}–Cr–Al triangular diagram from Barnes and Roeder (2001). References are as in Figs. 3 and 4. The detrital spinels from the Pavón Formation plot within the ocean floor fields (a) and within the flood basalts field (b).

these interpretations, the Western Precordillera Belt is composed of a late Proterozoic ophiolite (Davis et al., 1999), Ordovician basalts and pillow lavas interlayered with Caradoc wackes (Kay et al., 1984, 2005) which form a belt extending into the San Rafael block (Cingolani et al., 2000; see below), as well as late Silurian basaltic flows and dykes. More recently, the Chuscho Formation was also considered as part of the belt (Fauqué and Villar, 2003). This unit is interlayered with phyllites of the Ordovician Río Bonete Formation, and it is composed of diabase sills, basalts and tholeiitic pillow lavas. All these units were formed in different extensional settings and at different times (Davis et al., 1999, 2000). However, all have ε_{Nd} ranging from +6 to +9 (Kay et al., 2005) and were interpreted as E-MORB related (e.g. Kay et al., 1984). The northern part of the Western Precordillera Belt was interpreted as a segment of a transitional to plume-type mid-ocean ridge or unevolved back-arc basalts, whereas the southern part has a within-plate origin or a plume or plateau setting (Ramos et al., 2000 and references therein). Spinels and chromites were described from certain areas (Davis et al., 1999; Villar, 2003) but no chemical analyses are published. Although it is not possible to accept or reject this belt as a potential source area, the fact that some mafic rocks are interlayered with Caradoc clastic rocks suggests cannibalistic processes that reworked detritus (specifically chromian spinels) from the magmatic rocks into the sedimentary sequence. The high TiO_2 content of these volcanic rocks may support this argument.

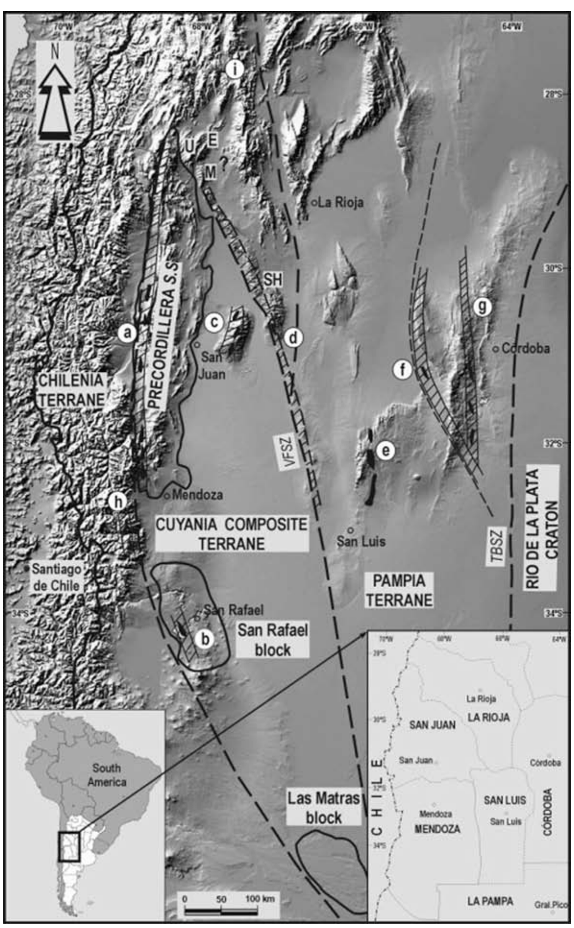

Fig. 8. Mafic to ultramafic belts considered as possible source areas of detrital chromian spinels. Terrane boundaries based on Ramos et al. (2000) and Porcher et al. (2004). a: Western Precordillera Belt; b: El Nihuil mafic body; c: Pie de Palo Belt; d: Valle Fértil Shear Zone; e: Virorco – Las Águilas Belt; f: Western Córdoba Belt; g: Eastern Córdoba Belt; h: Cordillera Frontal Belt; i: Fiambalá Range complex. In black: mafic and ultramafic outcrops; suture zones are marked by hatched lines while terrane boundaries by dashed lines. VFSZ = Valle Fértil Shear Zone; TBSZ = Trans-Brazilian Shear Zone; U = Umango Range; M = Maz Range; E = Espinal Range; SH = Sierra de la Huerta. Right side inset shows detail of the geographic location within Argentina and Chile.

(ii) In the San Rafael block, Mendoza province, a mafic body known as El Nihuil ('b' in Fig. 8) has been described (Cingolani et al., 2000). It is pre- to Upper-Ordovician with MORB affinities and contains ultramafic differentiates associated with tholeiitic diabases. Chromites were not described from these rocks. As the San Rafael block is a southern continuation of the Precordillera terrane, this mafic body was interpreted as a part of the Western Precordillera Belt (Haller and Ramos, 1984; Cingolani et al., 2000; 'a' in Fig. 8).

(iii) Pie de Palo Belt ('c' in Fig. 8), Western Pampeanas Ranges, San Juan province, where a Grenville-age ophiolite assemblage with island arc or back-arc affinities containing chromites and successively high contents of chromium have been described (Vujovich and Kay, 1998). This belt was interpreted as the amalgamation of the Precordillera and the Pie de Palo terranes (Cuyania composite terrane), before their accretion to Gondwana (Vujovich and Kay, 1998) or as part of pre-Famatinian autochthonous Gondwana (Casquet et al., 2006). It has been subjected to high-grade metamorphism. Although two main, different protoliths were distinguished (ultramafic cumulates and lava flows, both related to an arc environment), different rock types were associated to different oceanic settings and different crustal thicknesses: a magmatic arc on a thin continental crust or oceanic crust, a magmatic arc on a thick crust related to compression, or a magmatic arc and oceanic back-arc (Vujovich and Kay, 1996). No spinel chemistry is currently available for any of the lithologies. However, it is known that the ultramafic cumulate chromites are Cr-rich (Vujovich and Kay, 1998). Based on these facts, it is expected that the composition of the chromites would be rather different from those from the Pavón Formation. The unit with protolith lava flows has normal MORB characteristics, but no information about spinels content is available.

(iv) Valle Fértil shear zone ('d' in Fig. 8) is a lineament associated with mafic to ultramafic bodies. At Sierra de La Huerta (Western Pampeanas Ranges; see Fig. 8) a high grade metamorphic Precambrian to Lower Palaeozoic basement is composed of metasedimentary and meta-igneous rocks whose protoliths formed in an island arc or a back-arc (Vujovich and Kay, 1996). The mafic and ultramafic rocks contain green spinels with high Al, Fe and Mg contents but very low Cr. Some grains present a magnetite-rich rim due to metamorphism (Castro de Machuca et al., 1996). Therefore, they differ from the detrital spinels found in the Pavón Formation. The Umango, Maz and Espinal Ranges were considered part of the Western Pampeanas Ranges, although their association with the Precordillera terrane is still under investigation (Vujovich et al., 2005; Porcher et al., 2004). They are composed of amphibolites and rare ultramafic rocks and were interpreted as an arc or back-arc unit (Vujovich and Kay, 1996). However, some amphibolites were interpreted as less evolved lavas with transitional composition between alkaline and tholeiitic and from an intraplate or back-arc environment. Others are related to an oceanic arc developed on a continental crust. They are Grenville in age (Varela et al., 1996). No chromites have been described.

(v) Virorco – Las Águilas Belt, San Luis province ('e' in Fig. 8), where a mafic to ultramafic Precambrian to Palaeozoic layered intrusion is present. It contains chromian spinels classified by Ferracutti et al. (2004) according to Barnes and Roeder (2001) as crystallized in a mafic layered intrusion. Comparing the diagrams presented by Ferracutti et al. (2004) with the dataset from Pavón Formation, there is a clear difference between them, since our dataset shows less Al and more TiO_2 contents and less Fe^{2+}# for a given Cr#. Furthermore, the spinels from this belt show ferritchromite and chromium-rich magnetite rims produced by metamorphism (Ferracutti et al., 2004). According to von Gosen and Prozzi (1998), the mafic to ultramafic belt underwent several phases of metamorphism and deformation, reaching amphibolite facies during Middle to Late Ordovician.

(vi) Western Córdoba Belt ('f' in Fig. 8), where ultramafic serpentinised peridotites contain magmatic chromite, ferritchromite and spinels *sensu stricto*. These rocks underwent amphibolite to granulite facies metamorphism, but the spinels have preserved cores whose chemical compositions define them as from podiform bodies (Mutti et al., 2000). It should be noted that Pavón Formation lacks ferritchromite and spinels *s.s.* On the other hand, the chromites from the Western Córdoba Belt have a variable chemical composition (Cr_2O_3 = 11–47%, Al_2O_3 = 2–32%, total FeO = 18–81%, MgO 2–17%), and it should be ruled out as a source area.

(vii) In the Eastern Córdoba Belt ('g' in Fig. 8), there is an ophiolitic sequence developed in the Sierra Grande de Córdoba (Eastern Pampeanas Ranges) with chromian spinels, chromium-rich magnetite and iron-rich spinels, all of a magmatic origin and overprinted metamorphic characteristics. According to chromian spinels chemical data presented by Villar et al. (2001), they differ from the detrital grains found in the Pavón Formation mainly because the former have lower Cr_2O_3 (16–32%) and FeO (7–16%) contents and higher Al_2O_3 (38–48%) and MgO (15–20%) contents.

(viii) In the Cordillera Frontal ('h' in Fig. 8), the Guarguaráz Complex contains bodies of ultramafic serpentinised rocks fault-emplaced into a metasedimentary sequence (López and Gregori, 2004). These ultramafic rocks contain zoned spinels, which show a different composition in two different localities. At Las Tunas, the chromites have Zn-rich Al-chromite cores (interpreted as relict magmatic cores) and ferritchromite rims surrounded by outer Cr–magnetite rims, while those spinels from Salamanca (Cuchilla de Guarguaráz) district have a ferritchromite core and a chromium-rich magnetite rim (Bjerg et al., 1993). Although the metamorphism that affected these rocks is considered to be Devonian in age (which means after the deposition of the Pavón Formation), their cores are interpreted as relict magmatic, so they could still be used for comparison with the detrital grains from the Pavón Formation. Therefore, both groups of spinels are completely different from the detrital ones from the Pavón Formation. Tholeiitic basalts and metabasites with E-MORB affinities were also described in the Guarguaráz Complex. This complex was also considered the continuation of the Western Precordillera Belt (Haller and Ramos, 1984, and others), but provenance analyses indicate that the Guarguaráz Complex and equivalent units from the Precordillera terrane share a common evolution (López and Gregori, 2004).

(ix) The Early Cambrian gabbroic complex from the Fiambalá Range ('i' in Fig. 8) contains magmatic chromian spinels that were metamorphosed and has been interpreted as a stratified arc complex (Villar and Escayola, 1996). Chemical data presented by Villar et al. (2001) shows that their composition is characterized by very low Cr_2O_3 contents (3–6%), high Al_2O_3 (43–56%), low FeO and Fe_2O_3 (12–15% and 1.2%, respectively). Although they have similar MgO content compared with chromian spinels from Pavón wackes, they are different (see Table 1).

In summary, chemical analyses of spinels provided from the Valle Fértil shear zone, Virorco–Las Águilas Belt, Western and Eastern Córdoba Belts, Guarguaráz Complex of the Cordillera Frontal and the gabbroic complex from the Fiambalá Range show differences from the chemical composition of spinels from the Pavón Formation, making these rocks unlikely sources. On the other hand, the Western Precordillera Belt and its southern extension ('El Nihuil mafic body'), and the mafic rocks of the eastern side of the Precordillera (Pie de Palo Belt, Umango, Maz and Espinal Ranges) cannot be ruled out as sources. However, chemical analyses of the spinels described are needed, as well as a better knowledge of the mafic rocks within certain areas, to definitively either accept or reject these rocks as sources.

Palaeocurrents (not palinpastically restored) indicate an eastern provenance for the detritus of the Pavón Formation (Manassero et al., 1999), which therefore might point to a provenance from those sources located towards the east (present coordinates). Cingolani et al. (2003) also implied an eastern provenance for the Pavón basin. However, the spinels from Pavón Formation could result from cannibalistic processes of the lavas and sills interfingered with the clastic Caradoc rocks, meaning the mafic rocks outcropping to the west (Western Precordillera Belt and its southern extension). The 'El Nihuil mafic body' (Fig. 1) was tectonically emplaced and its primary relationship with the Pavón Formation sedimentary rocks is unknown. Nevertheless, its proximity to the basin might explain the subhedral character of the grains. The last possibility is to consider that the mafic and ultramafic source rocks of the detrital chromian spinels of the Pavón Formation were eroded away. Probable sources located farther afield are excluded based on grains shape, which suggest rather a short transport of detrital material. This is supported by petrography which indicates relatively high amounts of matrix and subangular to angular framework minerals (Cingolani et al., 2003), as well as by interpretations of the sequence as non-fan, sandy, marine turbidites deposited on a linear trough located close to the source areas and fed by turbidite and granular flows (Manassero et al., 1999).

7. Implications for the tectonic setting

The entire detrital chromian spinel dataset is subdivided into two different groups, notwithstanding their preferable volcanic origin and their association with an extensional tectonic environment. Group 1 is related to ocean floor basalts from a mid-ocean ridge, while Group 2 was derived from flood basalts in an oceanic or continental intraplate setting. No ages are presently available from the chromian spinel grains apart from their Caradoc minimum age. Therefore, each group may or may not represent different source rocks temporally separated from each other. Furthermore, the source area was not detected. It is important to note that both varieties of chromian spinels were found together within the same sampled layers.

Based on this information, it is possible to explain the compositional variations of the two groups of spinel in terms of tectonic evolution of the source area and associated host rocks. An extrusion of intraplate basalts occurred first, leading to the crystallization of spinels from Group 2, followed by a well-developed oceanic floor (Group 1) forming a mid-ocean ridge. More information is needed to support this, as the detrital grains could also come from two unrelated tectonic settings that were completely separated in time and space. However, it is known that continental flood basalts related to the break-up of continents have a wide range of TiO_2 content even within the same region depending on whether the mantle source is a plume or lithospheric mantle (Hisada et al., 1998).

This simple tectonic evolution represented by the chromian spinels could be correlated in a broad sense to those tectonic models that proposed a Laurentian origin for the Precordillera terrane. The microcontinent model assumes an initial rifting stage related to the opening of the Iapetus Ocean, followed by a well-developed oceanic crust leading to the separation of the Precordillera terrane from Laurentia (Astini et al., 1995; Thomas and Astini, 1996). If this were the case, then the initial host rocks of the detrital spinels from Pavón Formation would be within the units surrounding the Ouachita embayment. The more likely unit is the Catoctin Formation (ca. 570 Ma), which is composed of tholeiitic flood metabasalts as well as metarhyolites and scarce interlayered metasedimentary rocks (Aleinikoff et al., 1995). The unit is metamorphosed to greenschist facies and is related to the continental rifting and opening of the Iapetus Ocean (Badger and Sinha, 1988). However, these source areas would imply a western provenance that seems unlikely (Manassero et al., 1999; Cingolani et al., 2003).

On the other hand, the continental collision model (Dalla Salda et al., 1992) interpreted the Western Precordillera Belt (and its southern extension into the San Rafael block, known as the 'El Nihuil mafic body') as formed within the interior rift-basin through which Laurentia separated from Gondwana. However, as mentioned above, chemical analyses of the spinels from the Western Precordillera Belt are still needed and a provenance from an eastern source seems to be more likely (Manassero et al., 1999; Cingolani et al., 2003).

If an eastern provenance is assumed, the mafic and ultramafic rocks located on the eastern side of the Precordillera terrane are the most likely sources. Provenance from Gondwanan areas farther afield cannot be completely ruled out, but it is not likely due to the subhedral character of the detrital chromian spinels from the Pavón Formation, which along with petrography and facies analyses suggest rather a short transport. In this regard, it could be that either the Precordillera has a para-autochthonous origin (Aceñolaza et al., 2002; Finney et al., 2005, and others), or that the terrane collided with Gondwana prior to the Caradoc. The latter is emphasized when considering the Pie de Palo and probably other minor ranges such as Umango as part of autochthonous Gondwana prior to the lower Palaeozoic (Casquet et al., 2006). Lately, it could be speculated that the mafic source is no longer outcropping.

8. Conclusions

The early Caradoc Pavón Formation (Precordillera terrane) contains a low-diversity detrital heavy mineral population, characterized by a zircon-rich assemblage with minor but significant amounts of rutile and chromian spinels. Because these more stable heavy mineral phases can be recycled, a provenance from areas not closely related to the depositional basin cannot be excluded. However, the subhedral shape of the detrital spinels might indicate a close spatially-related source. The proposal of a mafic to ultramafic source that influenced the Pavón Formation chemistry can now be explained by the discovery of chromian spinels in the heavy mineral fraction.

These detrital chromian spinels are divided into two groups based on their chemical characteristics. Group 1 is characterized by intermediate Cr# values, low TiO_2, Fe^{3+}# and Fe^{2+}#, and indicates a mid-ocean ridge emplacement of their initial host rocks. Group 2 has Cr# values of ca. 0.7, high TiO_2, Fe^{3+}# and Fe^{2+}# and suggests an intraplate environment.

No known mafic to ultramafic rocks could be identified as the definite source. However, this case study shows a direct influence of two mafic sources shedding detrital heavy minerals into the Precordilleran Ordovician rocks. Chemical analyses of spinels from several probable source areas are needed to further constrain the provenance. However, a provenance from source rocks located toward the east (present coordinates) seems to be more likely, although an input from the Western Precordillera Belt (and its southern continuation within the San Rafael block) cannot be completely ruled out.

Notwithstanding the uncertainties and assuming a source located towards the east (present coordinates) and spatially closely related to the Pavón basin, the Precordillera terrane might have reached its present position before the Caradoc. However, neither the autochthonous nor the para-autochthonous models can be supported.

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