Geology and petrogenetic considerations of the Loma Marcelo skarn, Neoproterozoic basement of the Ventania System, Argentina

Carlos A. Ballivián Justiniano,a,f, Mabel E. Lanfranchini,a,g,⁎, Clemente Recío,b, Raúl E. de Barrio,c, Ana María Sato,c,f, Miguel A.S. Baseid, Marcio M. Pimentele, Ricardo O. Etcheverry,a,f, Colombo C.G. Tassinari,d

a Instituto de Recursos Minerales (INREMI), Universidad Nacional de La Plata-CIC, Calle 64 esquina 120, 1er piso, C.P. 1900 La Plata, Argentina
b Departamento de Geología, Facultad de Ciencias, Universidad de Salamanca, Plaza de los Cañidos s/n, 37008 Salamanca, Spain
c Centro de Investigaciones Geológicas (CIG), CONICET-Nacional de La Plata, Diagonal 113 N° 275, C.P. B1904DFR La Plata, Argentina
d Centro de Pesquisas Geocronológicas (CPGeo), Instituto de Geociências, Universidade de São Paulo, Cidade Universitária, Rua do Lago 562, CEP 05508-080 São Paulo, SP, Brazil
e Laboratório de Geocronologia, Instituto de Geociências, Universidade de Brasília, Campus Universitário Darcy Ribeiro, Asa Norte, CEP 70910-900 Brasília, DF, Brazil
f Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina

Abstract

The Late Precambrian–Early Palaeozoic crystalline basement of the Ventania System is mainly composed of Neoproterozoic S-type granites, Early Cambrian alkaline granites, and Middle Cambrian peralkaline rhyolites. The Neoproterozoic granites (ca. 607–581 Ma) crop out in the Cerro Pan de Azúcar-Cerro del Costral area and host the Loma Marcelo Ca/Mg skarn, composed of calc-silicate- and chondrodite-bearing assemblages. Petrographical, geochemical, and geochronological data indicate that the skarn was formed from carbonate xenoliths of sedimentary nature incorporated during the intrusion of the Neoproterozoic granites and that it is the result of three successive metamorphic events. The first one is related to the incorporation of carbonate xenoliths by the intrusion and the associated contact metamorphism. The second event is linked to the crystallization of the Early Cambrian granites and related post-magmatic processes. They are responsible for fluorine influx into the Neoproterozoic basement, which resulted in the formation of high-F minerals in the Loma Marcelo skarn (e.g. vesuvianite, chondrodite). The Sm-Nd garnet-whole rock isochron age of 526.8 ± 12.0 Ma in the skarn confirms its relationship with the Early Cambrian magmatism. The last event corresponds to a regional metamorphism assigned to the Late Devonian–Early Carboniferous on the basis of a LA-ICP-MS U-Pb age of 353.4 ± 6.7 Ma determined on zircons of the skarn as well as a Rb-Sr quartz-sericite isochron age of 364.4 ± 3.6 Ma obtained from a quartz vein that post-tectonically cuts the already mylonitized granites. The different chemical compositions of the carbonate protoliths determined the formation of two types of skarns of calcic and magnesian compositions. A single date of the calcic skarn defined a LA-ICP-MS U-Pb upper intercept age of 648 ± 21 Ma, providing the maximum sedimentation age for the calcic proolith of the Loma Marcelo skarn. The minimum sedimentation age is provided by the crystallization age of the S-type granite surrounding the skarn (ca. 607 Ma). The Loma Marcelo skarn reveals the occurrence of underground Neoproterozoic carbonate (meta-) sedimentary rocks as part of the basement of the Ventania System. These rocks could correlate with the carbonate sequences of the neighbouring Claromecó Basin and Tandilia System.

Keywords: Geochemistry, Geochronology, Carbonate protoliths, Polymetamorphism, Sierras Australes of Buenos Aires Province

Introduction

The Ventania System, or Sierras Australes of Buenos Aires Province, is located at the southeastern end of the South American Platform defined by de Almeida (1971) (Fig. 1a) in the southeastern part of the Buenos Aires Province, Argentina (Fig. 1b). It constitutes part of the "Bonaerense Positive" (Yrigoyen, 1975) along with the adjacent Claromecó Basin and the Tandilia System or Sierras Septentrionales of Buenos Aires Province (Fig. 1c). The Ventania System is mainly composed of Palaeozoic siliciclastic sedimentary rocks (Fig. 2), which were significant elements in the reconstruction of West Gondwana, and is considered as the conjugate margin of the Cape Fold Belt in South America (Fig. 3). The Ventania System is interpreted as a Neoproterozoic foreland basin which experienced loading and unloading phases during the assembly of Gondwana (Yrigoyen, 1975). The Neoproterozoic basement of the Ventania System is mainly composed of Palaeozoic siliciclastic sedimentary rocks (Fig. 2), which were significant elements in the reconstruction of West Gondwana, and is considered as the conjugate margin of the Cape Fold Belt in South America (Fig. 3).
Africa (Keidel, 1916; Du Toit, 1927). The crystalline basement of the Ventania System, which has a Neoproterozoic–Middle Cambrian age (Rapela et al., 2003; Tohver et al., 2012), crops out in different sectors along the western side of the system. It consists of granites, rhyolites, ignimbrites, and small bodies of andesitic, calc-silicate, and metacarbonate rocks (Fig. 2). K-Ar, Rb-Sr (Cingolani and Varela, 1973; Varela and Cingolani, 1976), and SHRIMP U-Pb (Rapela et al., 2003; Tohver et al., 2012) dating of the basement rocks from the Ventania System made it possible to assign the genesis of these rocks to the magmatic activity of the Brasiliano Orogenic Cycle.

The crystalline basement of the Ventania System is mainly composed of Neoproterozoic granites, Early Cambrian granites, and Middle Cambrian rhyolites. The Neoproterozoic basement crops out in the Cerro Pan de Azúcar-Cerro del Corral area (Fig. 2), one of the most deformed zones of the system. In this area, the basement units are lithologically diverse and involve a considerable structural complexity. They consist mainly of S-type granites and minor phenodacitic to phenorhyolitic rocks, a dyke-like andesitic body, and the Loma Marcelo skarn. The granites seem to be the continuity of the magmatism associated with the Dom Feliciano Belt of Brazil and Uruguay or alternatively with that of the Saldania Belt of South Africa (Rapela et al., 2003). Chemale et al. (2011) concluded that the correlation between the Dom Feliciano and Saldania belts is not direct due to the existence of geochronological and isotopic differences. The skarn consists of small bodies of calc-silicate and metacarbonate rocks spatially linked to the Neoproterozoic S-type granites.

Kilmurray (1968) defined the calc-silicate rocks from Loma Marcelo as skarn. He later indicated that calc-silicate and magnesian associations comprising the skarn were the result of metasomatism of calcareous relicts of the crystalline basement (Kilmurray, 1975). In agreement with Kilmurray (1968, 1975), Ballivián Justiniano et al. (2015) indicated that the Loma Marcelo skarn would be an indirect evidence of carbonate rocks at depth and additionally reported the occurrence of mineral associations corresponding to at least two overlapped metasomatic events.

The aim of this paper is to present new geochemical and geochronological data in order to propose the petrogenetic evolution of the Loma Marcelo skarn and to discuss the origin of the carbonate protoliths.

The geochemical results presented here allow the sedimentary nature of the carbonate protoliths of the skarn and the existence of at least three metamorphic events registered in the skarn to be established. New geochronological data allow one of these metamorphic events to be linked to the hydrothermal activity related to the Early Cambrian magmatism of the Ventania System. They also reveal the existence of a tectonometamorphic event of Late Devonian–Early Carboniferous age.

The results of this research are considered relevant at local and
regional scales since they contribute to the knowledge of the rocks present in the underground of the Ventania System. Specially, the skarn protoliths evidence their relation with the Neoproterozoic carbonate sedimentation of Southwest Gondwana.

2. Regional geologic setting

The Ventania System crystalline basement crops out along the western edge of the Sierra de Curamalal and in the adjacent plain that extends to the west (Fig. 2). It consists of granites at Cerro Pan de Azúcar, Cerro del Corral, Cerro San Mario, Cerro Colorado, and Estancia Agua Blanca; rhyolites at Cerro La Ermita and Estancia La Mascota; ignimbrites at Cerro del Corral; and andesite at Cerro Pan de Azúcar, and calc-silicate and metacarbonate rocks at Loma Marcelo. All of these rocks are deformed to different extents and are cut by post-tectonic quartz veins and veinlets.

Cingolani and Varela (1973) and Varela and Cingolani (1976) performed the first K-Ar and Rb-Sr systematic dating of the Ventania System basement rocks. The ages obtained spanned from the Cryogenian to the Late Triassic. The post-Cambrian ages obtained in the basement rocks would be the result of partial or total opening of the K-Ar and Rb-Sr isotopic systems caused by the Neopaleozoic deformation and its related warming and fluid circulation (von Gosen et al., 1990). In this sense, former K-Ar and Rb-Sr ages are interpreted as minimum ages.

Petrological and SHRIMP U-Pb zircon data (Rapela et al., 2003; Gregori et al., 2005; Tohver et al., 2012) allow three stages of magmatic activity to be distinguished in the basement:

1) The first stage, of Ediacaran age (ca. 607–581 Ma), is represented by the S-type granites of the Cerro Pan de Azúcar-Cerro del Corral area. It is related to the collisional orogeny responsible for the closure of the Adamastor Ocean (Hartnady et al., 1985), a restricted ocean located between South America and Africa. Its closure was linked to the assembly of West Gondwana (Cordani et al., 2013).

2) The second stage corresponds to a magmatic event of Early Cambrian age (ca. 533–524 Ma), which is associated with the collapse of the Neoproterozoic collisional orogen. It is represented by the alkaline granites of Cerro Colorado and Estancia Agua Blanca and by the calc-alkaline granite of Cerro San Mario (Fig. 2).

3) The third stage, of Middle Cambrian age (ca. 509–505 Ma), is represented by the peralkaline rhyolites of Cerro La Ermita and Estancia La Mascota (Fig. 2), which are associated with the emplacement of a thermal anomaly (mantle plume or mafic underplate).

The sedimentary cover of the Ventania System comprises three sedimentary units (Harrington, 1947): Curamalal (Late Cambrian–Ordovician), Ventana (Silurian–Devonian), and Pillahuincó (Carboniferous–Permian) groups (Fig. 2). The Curamalal and Ventana groups represent stable platform sedimentary sequences (Andres et al., 1989) mainly composed of quartzites and sandstones with minor basal conglomerates and cuspidal pelites. Although some authors proposed that the Curamalal and Ventana groups may be the same tectonically repeated unit (Kilmurray, 1975; Tomozzi and Cristallini, 2004), there is currently general agreement regarding the validity of the original scheme proposed by Harrington (1947), which

Fig. 2. Geological map of the Ventania System (modified from Ramos et al. (2014)).
considered them as two separate units. The sedimentary rocks of the Pillahuincó Group crop out in Sierra de las Tunas and Sierra de Pillahuincó, along the eastern sector of the Ventania System. In addition, they extend towards the underground between the Ventania and Tandilia systems, where they are part of the infilling of the Claromecó Basin. The main rock types that comprise the Pillahuincó Group are diamicrites, conglomerates, quartzites, arkoses, and dark grey pelites of glacialmarine and fluvo-deltaic environments (Andreas et al., 1989) and minor intercalations of tuff horizons (Iñiguez et al., 1988). Geophysical and drilling data allowed the offshore continuity of at least part of the sedimentary sequence to be identified (Pángaro and Ramos, 2012; Pángaro et al., 2016). There is no evidence of igneous activity affecting the Palaeozoic sedimentary sequence of the Ventania System.

On the basis of detrital zircon provenance studies, the most likely source areas of the Curamalal and Ventana groups are Tandilia System and Sierras Pampeanas of central-west Argentina (Uriz et al., 2011; Ramos et al., 2014). The main source of the Pillahuincó Group was the magmatic arc proposed by Ramos (2008) for Northern Patagonia along the Común Curá Massif. Ramos et al. (2014) also proposed the same magmatic arc as the source of the pyroclastic materials interbedded in the upper section of the Pillahuincó Group.

Both the crystalline basement (mylonitized) and the Palaeozoic sedimentary cover (folded and faulted) are deformed. The conspicuous structural feature of the Ventania System is the strong folding that affects the Palaeozoic sequence. The axial planes mostly verge to the NE (Harrington, 1947), the direction in which a decrease in the intensity of folding and metamorphic grade is also observed (von Gosen et al., 1990, 1991). The Ventania System was considered as an example of pure folding for decades (e.g. Harrington, 1947, 1970, 1972; Llambías and Frozzi, 1975). However, Schiller (1930) had already highlighted the importance of faulting in structuring the system. Varela et al. (1986), von Gosen et al. (1990), Cobbold et al. (1991), and Tomezzoli and Cristalli (1988) also supported this observation.

The deformation was considered to be of Permain–Early Triassic age on the basis of stratigraphic and structural criteria (e.g. Varela et al., 1985; Cobbold et al., 1986; Buggisch, 1987; von Gosen et al., 1990; López-Gamundi et al., 1995; Rossello et al., 1997). K-Ar dating on illites from the Curamalal Group yielded ages ranging from 282 ± 3 to 257 ± 8 Ma (Varela et al., 1985; Buggisch, 1987), which allowed the deformation to be assigned to the San Rafael Orogenic Phase (Arcuy and Caminos, 1987). Subsequent palaeomagnetic studies performed in the top unit of the Pillahuincó Group revealed that the lower part of the unit was deposited, deformed, and magnetized during the Early Permian (Tomezzoli, 1999, 2001; Tomezzoli and Vilas, 1999). Some authors argue that the deformation occurred in a unique phase during the Late Permian–Early Triassic (e.g. Japas, 1987), while others suggest that it took place in several phases during the Late Devonian–Early Carboniferous to the Permian (e.g. Massabie and Rossello, 1984; Tomezzoli, 2012).

3. Geology of the Cerro Pan de Azúcar-Cerro del Corral area

Cerro Pan de Azúcar and Cerro del Corral represent the SW and NE flanks, respectively, of a faulted overturned antcline along whose axis the erosive processes formed the Abra Meyer Valley (Varela et al., 1986). This narrow valley constitutes an erosive window that allows the basement rocks that underlie the Eopalaeozoic sedimentary rocks of La Lолa and Mascota formations of the Curamalal Group to be recognized (Harrington, 1947) (Fig. 3). The name “Sauce Chico Inlier” is proposed here for this erosive window, alluding to the Sauce Chico Group, a stratigraphic unit defined by Cueroa et al. (1975) to designate the basement rocks that crop out in the Cerro Pan de Azúcar-Cerro del Corral area. The crystalline basement consists of cataclastic and mylonitic granites, mylonitic ignimbrites, a meta-andesite, and the Loma Marcelo scharn (Fig. 3). These rocks are the most deformed of the Ventania System, Delpino and Dimieri (1992) and Delpino (1993) point out that the deformation and metamorphism would have reached temperatures ranging from 400 to 450 °C and pressures of about 200 MPa, conditions corresponding to the greenschist facies.

The meta-igneous rocks of the NE slope of Cerro Pan de Azúcar underlie the conglomerates and quartzites of La Lola and Mascota formations, respectively. These rocks are in normal position, and no evidence of intrusive contact between them and the meta-igneous rocks has been found (von Gosen et al., 1990). Cobbold et al. (1986) and Gregori et al. (2005) indicated that the contact between the crystalline basement and the overlying sedimentary cover is a thrust fault with a NE vergence, consistent with the tectonic nature attributed to this contact by Schiller (1930) and Cucchi (1966). The granitic ultramylonite belt, which allows a fault of N 340°/60° SW orientation to be inferred at Cerro Pan de Azúcar, is almost completely covered by debris from La Lola and Mascota formations and would not constitute the primary contact between the crystalline basement and the Palaeozoic sedimentary cover (Figs. 3 and 4). Less than 1.5 km to the NE from Cerro del Corral, the Mascota Formation crops out directly over the granitic mylonites. Consequently, the basement-Palaeozoic cover contact would be an angular unconformity or a disconformity.

At Cerro del Corral, two N-S trending and west dipping shear zones with granitic and ignimbritic ultramylonites represent the tectonic contact between granite, ignimbrite, and La Lолa Formation (Figs. 3 and 4). These shear zones converge toward the north, becoming a single fault with a N-S trend that tectonically juxtaposes the granite of Cerro 21 de Septiembre against La Lola Formation. Along the Cerro del Hueco-Cerro del Corral belt, the sedimentary sequence is inverted due to the overturning of the anticline towards the NE and La Lola Formation conglomeratic pebbles are deformed under ductile conditions (Schiller, 1930; Cucchi, 1966).

In the Sauce Chico Inlier, the NW–SE to N–S trending mylonitic foliation dips between 30 and 90° to the SW–W, whereas the associated stretching lineation dips 47° to the SSE (Fig. 4). The kinematic indicators reveal reverse dextral shearing with a top-to-NNW hanging wall. Post-tectonic quartz veins and veinlets (∓ sericite, calcite, epidote, galena, and/or oxides) are discordant as well as parallel to the mylonitic foliation.

The Sauce Chico Inlier granites are cataclastic and mylonitic syenogranites and monzogranites characterized by heterogeneity and variation in colour and grain size (Fig. 5a, b). The less deformed granites of the area, which preserve the igneous primary features (e.g. equigranular texture), were identified at Loma Marcelo. The variable amount of sericite, chlorite, and muscovite of the matrix defines the schistosity of the granitic mylonites. SHRIMP U–Pb zircon dating revealed crystallization ages of 607.0 ± 5.2 Ma for the Cerro del Corral granite (Rapela et al., 2003) and 580.8 ± 7.9 Ma for the Cerro Pan de Azúcar granite (Tohver et al., 2012). In addition, Tohver et al. (2012) reported a muscovite Ar-Ar age of 581 ± 5 Ma for the Cerro del Corral granite. These results indicate a Neoproterozoic timing for the Cerro Pan de Azúcar-Cerro del Corral granite emplacement.

The mylonitic ignimbrite of the Sauce Chico Inlier, of phanerodacitic to phonolitic composition, crops out in the eastern half of Cerro del Corral (Figs. 3 and 5c). It exhibits quartz and feldspar crystalloclasts (maximum length of 3–4 mm) immersed in a reddish-brown to greenish-grey aphanitic matrix (Fig. 5d) and has a texture marked by lens-shaped, greenish-grey fiammes (González et al., 2004). The contacts between ignimbrite, granite, and La Lola Formation are tectonic (Figs. 3 and 5c). Therefore, field relationships do not allow determination of the relative age of the ignimbrite, which could be either older than the granite and a roof-pendant or younger and deposited on it. However, based on geochemical similarities, Ballivián Justiniano (2016) correlated the ignimbrite of Cerro del Corral with the alkaline granites of Cerro Colorado and Estancia Agua Blanca.

The meta-andesite of the Sauce Chico Inlier crops out
discontinuously in the NE slope of Cerro Pan de Azúcar (Figs. 3 and 5e).
The largest outcrop is 80 m long and 30 m wide. The andesite has a
porphyritic texture with large phenocrysts of greyish-white plagioclase,
up to 4 cm in length, on a dark green aphanitic groundmass (Fig. 5f).
The andesite shows a pervasive foliation and its contact with the
granitic rock, also foliated, is obscured by the deformation. Despite its
elongated dyke-like shape and concordant relationship with the
mylonitic foliation, unpublished magnetometric data do not show
continuity of the main andesitic outcrop at depth, suggesting that it
could be a roof-pendant. The porphyritic texture and vesicles are typical
igneous features of shallow magma emplacement, thus indicating that the meta-andesite is either a lava flow or a subvolcanic body. Calc-silicate and metacarbonate rocks that constitute de skarn crop out discontinuously at the Loma Marcelo area, a small hill of about 0.12 km² (Fig. 6). Its host rock is mainly composed of cataclastic and protomylonitic granites intercalated with highly schistose belts of granitic mylonites. Calc-silicate rocks (calcic skarn) crop out, aligned in a NNW–SSE trend along 175 m in the central-western sector of the hill. The largest calc-silicate outcrop, 10 m long and 5 m wide, is lenticular in shape (LM-9 in Fig. 6). A metacarbonate rock (magnesian skarn), also of lenticular shape, is 2.8 m long and 2.2 m wide and crops out in the western side of the hill (LM-6 in Fig. 6). The calc-silicate and metacarbonate rocks constitute the Loma Marcelo skarn and are the study object of this paper.

4. Materials and methods

The lithogeochemical characterization was carried out on granite and skarn samples from the Sauce Chico Inlier. Major and trace elements were analysed by inductively coupled plasma mass spectrometry (ICP-MS) at Bureau Veritas Minerals Laboratories, Canada. The C and S contents were determined by infrared detection following combustion in a LECO analyser, whereas the F contents were determined by the potentiometric method with a LaF crystal membrane electrode. Electron microprobe analyses were performed at two laboratories: 1) Departamento de Geología, Universidad de Oviedo, Spain, with a CAMECA Camebax SX-100 microprobe, and 2) Laboratorio de Microscopía Electrónica y Análisis por Rayos X (LAMARX), Universidad Nacional de Córdoba, Argentina, with a JEOL Superprobe JXA-8230 microprobe. Crystals of garnet, pyroxene, vesuvianite, titanite, chondrodite, and spinel from the Loma Marcelo skarn were analysed using a current acceleration of 15 kV, an electric current between 10 and 20 nA, and a beam diameter of 1–2 μm. Calibrations were performed using natural and synthetic standards.

One sample of the calcic skarn (11415, LM-9) was selected for laser ablation (LA)-ICP-MS U-Pb zircon dating. It was not possible to separate zircon grains from samples of the magnesian skarn. Concentration and separation of zircon grains were done at the Centro de Investigaciones Geológicas (CIG, CONICET-UNLP). A sample of 10 kg was crushed, washed, milled, and sieved. The heavy minerals were concentrated with a pan and then treated with a handheld magnet and Frantz isodynamic magnetic separator to concentrate the non-magnetic fraction. Zircon grains were handpicked in alcohol under a binocular microscope. The U-Pb ages were obtained at the Centro de Pesquisas Geocronológicas (CPGeo), Universidade de São Paulo, Brazil, using a Thermo Fisher Neptune LA multicollector ICP-MS equipped with a 193 Photon laser system, following the analytical method described by Sato et al. (2010). Prior to LA-ICP-MS U-Pb analyses, the selected zircon grains were mounted in epoxy resin and their internal structure was exposed by polishing for dating.

Sm-Nd isotopic dating was performed at the Laboratório de Geocronologia, Universidade de Brasília, Brazil, on garnet-whole rock pairs of skarn samples 11415 and 19240 (both from LM-9) following the method described by Gioia and Pimentel (2000). The garnet and whole rock samples were finely powdered and their Sm and Nd contents were determined by X-ray fluorescence. Sm and Nd were extracted following conventional cation exchange techniques and then loaded on Re evaporation filaments of double filament assemblies. The isotopic measurements were carried out on a multicollector Finnigan MAT 262.
mass spectrometer in static mode. The uncertainties for the $^{147}$Sm/$^{144}$Nd and $^{143}$Nd/$^{144}$Nd ratios are better than ± 0.2% (2σ) and ± 0.005% (2σ), respectively. $^{143}$Nd/$^{144}$Nd ratios were normalized to an $^{146}$Nd/$^{144}$Nd ratio of 0.7219 and the decay constant used was $\lambda^{147}$Sm = 6.54 × 10$^{-12}$ a$^{-1}$.

Rb-Sr isotopic dating was performed at the Centro de Pesquisas Geocronológicas, Universidade de São Paulo, Brazil, on a quartz-sericite pair of a vein that post-tectonically cuts the granitic mylonites of Loma Marcelo (sample 1819), following the method described by Kawashita (1972), as modified by Sato et al. (1995). The quartz and sericite samples were finely powdered and analysed by the isotope dilution method for determination of their Rb and Sr contents and $^{87}$Sr/$^{86}$Sr ratios. The isotopic measurements were carried out on a multicollector VG-354 thermionic mass spectrometer using a Daly amplifier. Uncertainties are presented at 1σ level for $^{87}$Rb/$^{86}$Sr and at 2σ level for $^{87}$Sr/$^{86}$Sr. $^{87}$Sr/$^{86}$Sr ratios were normalized to an $^{86}$Sr/$^{88}$Sr ratio of 0.1194 and the decay constant used was $\lambda^{87}$Rb = 1.42 × 10$^{-11}$ a$^{-1}$.

The results of the Rb-Sr, Sm-Nd, and U-Pb analyses were plotted with Isoplot 4.15 (Ludwig, 2008).

Oxygen stable isotope determinations in silicates and oxides were performed at the Servicio General de Análisis de Isótopos Estables, Universidad de Salamanca, Spain. The analysed minerals were handpicked under a binocular microscope. The extraction of O$_2$ from garnet, pyroxene, wollastonite, vesuvianite, chondrodite, and spinel from the Loma Marcelo skarn for isotopic analysis was performed by laser fluorination (Clayton and Mayeda, 1963), employing a Synrad 25 W CO$_2$ laser (Sharp, 1990) and reacting mineral powders with ClF$_3$ reagent (e.g. Borthwick and Harmon, 1982). Isotope ratios were measured on a VG-Isotech SIRA-II dual inlet mass spectrometer. Both internal and international reference standards (NBS-28, NBS-30) were run to check accuracy and precision. Results are reported in δ$^{18}$O notation relative to the Vienna Standard Mean Ocean Water (V-SMOW) using a δ$^{18}$O value of 9.6‰ for NBS-28 (quartz) for the mass spectrometer calibration. The long-term reproducibility for repeated determination of reference samples was better than ± 0.2‰ (1σ).

5. Petrography and mineral composition

5.1. Sauce Chico Inlier granites

The Neoproterozoic granitic cataclasites and mylonites are the more widely exposed rocks in the Sauce Chico Inlier. They crop out in the NE slope of Cerro Pan de Azúcar, the western half of Cerro del Corral, Cerro 21 de Septiembre, and Loma Marcelo (Fig. 3).

5.1.1. Cataclastic granites

The cataclastic syenogranites are grey and medium to coarse grained (Fig.7a); a variety of coarse to very coarse grained granite was also identified. These granites are mainly composed of quartz, microcline, oligoclase, biotite, muscovite, and sericite (Fig. 7b). These are the rocks where the original protolith texture is better preserved. Quartz crystals show dynamic and static recrystallization features. They are up to 2 mm in length and are small subhedral to euhedral crystals, approximately 40 μm in diameter, with polygonal granoblastic texture (Fig. 7a, b).

Anhedral to subhedral feldspar crystals have millimetric size (Fig.7b). Microcline sometimes displays curved cross-hatched twinning and patches due to albite exsolution. The plagioclase (oligoclase, An$_{14}$)
shows curved and kinked polysynthetic twinning or antiperthites in the form of parallel veins.

Biotite and muscovite are scarce and are arranged in curved patterns that contour the quartz and feldspar crystals. Accessory minerals such as apatite, zircon, magnetite, epidote, and calcite were observed.

5.1.2. Granitic mylonites

The Sauce Chico Inlier granitic mylonites are brownish-red, greenish-grey, or green in colour and have been classified as protomylonites, mylonites, and ultramylonites. The protomylonites and mylonites are the dominant rocks (Fig. 7c), while the ultramylonites constitute discrete belts coincident with the ductile faults (Fig. 7d). Rhomboidal, lenticular, or banded porphyroclasts of the syenogranitic protolith are commonly included in the mylonitic matrix of protomylonites and mylonites (Fig. 7e).

The protomylonitic granites consist of quartz-feldspathic porphyroclasts settled in a matrix predominantly composed of sercite, chlorite, and muscovite, along with minor biotite, quartz, and feldspar. The mylonites have abundant micaceous minerals and scarce porphyroclasts of feldspar. In both protomylonites and mylonites, fractured crystals of garnet can also be observed (Fig. 7f). Accessory minerals are apatite, zircon, magnetite, and epidote.

The ultramylonites are fine-grained rocks with continuous foliation defined by preferentially oriented muscovite, chlorite, sercite, and quartz grains (Fig. 7g). The transition between the different types of mylonites is sharp, reflecting strong gradients in the intensity of the deformation. Evidences of pressure dissolution, intracrystalline deformation, recovery, and recrystallization processes were observed.

The pressure dissolution and the subsequent redeposition of the dissolved material are evidenced by pressure shadows and dark bands of insoluble materials concentrated along the mylonitic foliation. The intracrystalline deformation and recovery are mainly evidenced by undulating extinction, deformation lamellae, and deformation bands in the quartz crystals. The deformation mechanisms identified in the granitic mylonites suggest low-grade metamorphic conditions during mylonitization (temperature between 350 and 400 °C, lower part of the greenschist facies).

Shear sense indicators are C- and C’-type shear bands (Fig. 7h), oblique foliation in quartz, sigma-type mantled feldspars, mica
fish (muscovite), and boudinated and domino-type magnetite porphyroclasts. All of these indicate that the granites of the Sauce Chico Inlier, like the other basement rocks, were affected by dextral shearing.

5.2. Loma Marcelo skarn

5.2.1. Calc-silicate rocks (calcic skarn)

Boudins of calc-silicate rocks are aligned parallel to the mylonitic foliation of the metagranites (Fig. 6). The colour of calc-silicate rocks is very variable (Fig. 8), ranging from greyish white and reddish pink to greyish green. They are composed of garnet, clinopyroxene, scapolite, plagioclase, wollastonite, vesuvianite, and calcite, among other minerals. The grain size is medium to coarse and the textures vary from granoblastic to porphyroblastic.

Garnets were classified into three types, named 1, 2, and 3 (Ballivián Justiniano et al., 2015) (Fig. 8a, b, e–g). Type 1 garnet consists of subhedral to euhedral crystals with diameters of up to 500 μm, anomalous anisotropy, and hourglass-shaped twins. Type 2 garnet forms irregular centimetric masses with anomalous anisotropy and strong fracturing. Some subhedral to euhedral crystals with oscillatory zoning were identified within the masses. Type 3 garnet forms mosaics of euhedral dodecahedral crystals approximately 100 μm in diameter, completely isotropic, and scarcely fractured. Crystals of type 3 garnet were also identified inside irregular cavities, together with calcite and/or quartz.

Two types of clinopyroxene, of dark green and light green colours, were clearly identified in hand specimens (Ballivián Justiniano et al., 2015) (Fig. 8c). Dark green clinopyroxene is anhedral and subrounded and has maximum lengths of approximately 4 mm. The light green clinopyroxene appears as subhedral to euhedral crystals and reaches lengths of up to 6–7 mm. The dark green clinopyroxene is more altered and fractured than the light green one. The different types of pyroxene and garnet are part of a different paragenesis, which will be discussed in Section 9.1.

Scapolite and plagioclase were identified as meionite and bytownite, respectively. Wollastonite is recognized by its fibrous habit (Fig. 8d). The vesuvianite appears in four varieties, coloured green, brownish green, brown, and blue (Fig. 8d). The green and brown
varieties exhibit radiating-prismatic habit, while the blue one is interstitial and very scarce.

The matrix is scarce and composed of calcite that ranges from 1 to 2 mm in diameter (Fig. 8h) with granoblastic texture. Titanite is a frequent retrograde mineral that often exhibits concentric zonation. Quartz, epidote, apatite, and zircon are present as minor constituents. Galena is a minor component in a quartz veinlet that cuts the calc-silicate rocks.

A millimetre-wide banding was identified in the calc-silicate rocks, consisting of whitish bands that are mainly composed of calcite and/or wollastonite, interspersed with reddish and greenish bands composed of garnet and clinopyroxene. In addition, a penetrative foliation of NW–SE/85–90° SW orientation was recognized, together with the existence of lattice-preferred orientation in calcite crystals of the skarn matrix (Ballivián Justiniano et al., 2015).

Electron microprobe analysis allowed garnets to be classified as grandite and clinopyroxenes as salite. Type 1 garnet is andraditic grossular (Grs 75.54–91.84% Adr 4.08–21.39%), whereas the type 2 (Grs 80.03–98.84% Adr 0.05–9.71%) and type 3 garnets (Grs 90.03–98.84% Adr 0.00–9.71%) are more grossularitic (Fig. 9a; Supplementary Material 1). The dark green clinopyroxene is diopsidic hedenbergite (Di 67.90–81.25% Hd 17.88–31.34%) (Fig. 9b; Supplementary Material 2). The green and brown colours of the vesuvianites are a consequence of their different contents of Fe and Ti, in agreement with the observations made by Manning (1975). The green vesuvianite has high FeO (4.06–5.34%) and low TiO2 (≤ 2.12%) contents, while the brown vesuvianite has slightly lower contents of FeO (3.51–5.34%) and TiO2 contents of up to 3.82% (Fig. 9c; Supplementary Material 3). The blue vesuvianite could not be analysed by electron microprobe because of its small grain size; however, its colour could be due to the occurrence of small amounts of Cu (Fitzgerald et al., 1986). The F content reaches up to 2.70%. The titanite crystals present compositional zoning, with low-F cores (1.73%) and more enriched rims (2.12–2.47%) (Fig. 9d, e; Supplementary Material 4).

5.2.2. Metacarbonate rock (magnesian skarn)

The metacarbonate rock is found in the western sector of Loma Marcelo. It is mainly composed of chondrodite and spinel porphyroblasts included in a calcite + dolomite matrix with granoblastic texture and dynamic recrystallization of grain boundaries (Fig. 10a).

Chondrodite is pale yellow to orange-yellow in hand specimens and exhibits orange fluorescence under short-wave ultraviolet light (Fig. 10b). The chondrodite crystals are anhedral and slightly elongated (≤ 8 mm); they are intensely fractured and have high relief and simple or polysynthetic twins (Fig. 10c). Spinel is bluish grey to violet, subhedral to euhedral, and reaches diameters of up to 3 mm (Fig. 10d, f). The crystals of chondrodite and spinel are incipiently replaced by dozyite [(Mg2Al2)(Si4Al2)O15(OH)12] and these three minerals show a variable degree of serpentinization. Dozyite has laminar habit, perfect cleavage, and undulately extinction (Fig. 10e). In addition, fluorite grains were identified within fractures and along the grain boundaries of chondrodite, spinel, and dozyite crystals (Fig. 10f). Other minerals identified are quartz and small inclusions of pyrite and Co-pyrite inside chondrodite crystals.
The general formula of the Loma Marcelo skarn chondrodite can be expressed as \((\text{Mg}_{4.74} \text{Fe}^{2+}_{0.03} \text{Ti}^{4+}_{0.006} \text{Mn}^{2+}_{0.005})_{\Sigma} = 4.78 \text{Si}_{1.84} \text{O}_{4} (\text{OH}_{0.49} \text{F}_{1.51})_{\Sigma} = 2.00\) (Supplementary Material 5). Note the high F content (8.69% on average). Neither other humite-group minerals nor forsterite were identified by X-ray diffraction analysis or electron microprobe in samples of the metacarbonate rock.

The spinel of the metacarbonate rock consists mainly of spinel sensu stricto (Spl 95.86–97.12%). The replacement of Mg by Fe\(^{2+}\), Mn, and Zn is reduced, with the molecular proportions of hercynite, galaxite, and gahnite being less than 5%. The general formula of the Loma Marcelo skarn spinel can be expressed as \((\text{Mg}_{7.64} \text{Fe}^{2+}_{0.27} \text{Mn}_{0.02} \text{Zn}_{0.008})_{\Sigma} = 7.94 (\text{Al}_{15.99} \text{Fe}^{3+}_{0.01} \text{Cr}_{0.009})_{\Sigma} = 16.00 \text{O}_{32}\) (Supplementary Material 6).

6. Lithogeochemistry

Major and trace elements were determined in granite and skarn samples from the Sauce Chico Inlier. The complete results of the analysed samples are presented in Supplementary Material 7 and 8.

6.1. Sauce Chico Inlier granites

The cataclastic granites (samples 11413 and 19245) from Loma Marcelo have 73–74% SiO\(_2\) and plot within the sub-alkaline field of the SiO\(_2\)-alkalis diagram of Irvine and Baragar (1971). These rocks are peraluminous, with values of the alumina saturation index \(\text{ASI} = \text{molal Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})\) of 1.09 and 1.17 and normative corundum of 1.38 and 2.33% (Supplementary Material 7). The cataclastic granites are the less deformed granitic rocks at the Sauce Chico Inlier. When plotted using the Ab-An-Or diagram (Barker, 1979), the analysed samples fall within the granite field (Fig. 11a).

Primitive mantle-normalized spidergrams of cataclastic granite samples exhibit a marked enrichment in incompatible elements with respect to the most compatible elements, as well as negative anomalies of Th, U, Nb, and Ta and positive anomalies of Rb, K, Pb, and Eu (Fig. 11b). The total REE reaches 49.86–64.95 ppm (Supplementary Material 7). Chondrite-normalized REE patterns indicate strong enrichment of LREE \((\text{La}_N/\text{Lu}_N = 36.74 \text{ and } 149.47)\) and positive Eu anomalies \((\text{Eu} / \text{Eu}^{*} = 2.81 \text{ and } 3.07)\) (Fig. 11c). In relation to the REE pattern of the upper crust, that of the cataclastic granites exhibits a similar Eu concentration and is slightly depleted in the other REE.

The analysed samples of granitic mylonite (19198 and CPA-1) from Loma Marcelo and Cerro Pan de Azúcar have lower SiO\(_2\), Na\(_2\)O, and K\(_2\)O contents and higher contents of the other oxides and loss on ignition (LOI) relative to the cataclastic granites (Supplementary Material 7). These mylonites plot within the sub-alkaline field of the SiO\(_2\)-alkalis diagram and are peraluminous, with alumina saturation index of 1.10 and 3.17 and normative corundum contents of 1.64 and 15.58% (Supplementary Material 7).

Primitive mantle-normalized spidergrams of granitic mylonite samples are similar to those of the cataclastic granites; however, granitic mylonites have a slightly higher content of HREE. The total REE reaches 159.89–180.61 ppm (Supplementary Material 7). In relation to the cataclastic granites, the chondrite-normalized REE patterns of the granitic mylonites show similar slopes for the LREE and flatter slopes for the HREE \((\text{La}_N/\text{Lu}_N = 7.29 \text{ and } 17.69)\) (Fig. 11c). The Eu anomalies are negative \((\text{Eu} / \text{Eu}^{*} = 0.60 \text{ and } 0.72)\) and the general REE patterns are identical to those of the upper crust.

When plotted in tectonic discrimination diagrams, the cataclastic granite and granitic mylonite samples fall within the volcanic arc and syncollisional fields of the Y-Nb and Yb-Ta diagrams of Pearce et al. (1984) (Fig. 11d) and in the S-I-type field of the Ga/Al versus Zr diagram of Whalen et al. (1987) (Fig. 11e).
The cataclastic granites have positive Eu anomalies and smaller REE contents than the granitic mylonites analysed by Gregori et al. (2005) (Fig. 11c). The geochemical characteristics of cataclastic granites would respond to primary igneous features resulting from their collisional genesis, interpreted by Rapela et al. (2003) as the closure of the Adamastor Ocean during the Neoproterozoic. The strong enrichment of LREE suggests that garnet remained as a residual phase during melting of the parent rocks. The positive Eu anomalies can be explained by crystallization of plagioclase from a liquid relatively impoverished in Eu due to prior fractionation of this element at the source (Korhonen et al., 2010).

An εNd value of −9.2 and a depleted mantle model age of 1974 Ma suggest a Palaeoproterozoic crustal component in the source region of the Neoproterozoic. The strong enrichment of LREE suggests that garnet remained as a residual phase during melting of the parent rocks. The positive Eu anomalies can be explained by crystallization of plagioclase from a liquid relatively impoverished in Eu due to prior fractionation of this element at the source (Korhonen et al., 2010).

6.2. Loma Marcelo skarn

The metasomatic influx of chemical elements into the carbonate system resulted in a calcic skarn (calc-silicate rocks) and a magnesian skarn (metacarbonate rock), depending on the different compositions of carbonate protoliths. The two types of skarns have similar CaO contents but different amounts of SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MgO and LOI, and low contents of Cr₂O₃, MnO, Na₂O, K₂O, and P₂O₅ (Figs. 12 and 13 a, b; Supplementary Material 7). Contents of 0.76–1.99% C, less than 0.02% S, and about 0.27% F were detected in the calcic skarn. On the other hand, contents of 7.45–9.10% C, less than 0.05% S, and 1.69% F were identified in the magnesian skarn. In the calcic skarn, Ca, Al, Fe, and Mg are concentrated in the silicate minerals (e.g. garnet, clinopyroxene, wollastonite, and vesuvianite), whereas in the magnesian skarn, Ca is concentrated in the carbonate matrix (mainly of calcitic composition) and Mg in the chondrodite and spinel. Very low concentrations of elements of economic interest (e.g. precious and base metals) were detected in both skarn types (Supplementary Material 7).

The variability of SiO₂ and LOI (Supplementary Material 7) in the
calcic and magnesian skarns is due to their different proportions of silicate and carbonate minerals. There is an inverse relationship between the two variables: high SiO₂ contents are related to low LOI contents, which is linked to the fact that the greater the proportion of silicates, the smaller the proportion of carbonates. The silicates and carbonates constitute 88.0 and 12.0% of the calcic skarn, respectively, whereas they represent 32.5 and 67.5% of the magnesian skarn. The lower percentages of carbonates would be a consequence of the consumption of calcite and quartz by the majority of the reactions triggered during the prograde metamorphism and the concomitant decrease in the modal content of both minerals. In this way, this rock would have lost much of its carbonate minerals, turning into a calc-silicate rock.

Dolomitic protoliths are generally Fe-poor, and ferromagnesian minerals of their metamorphic equivalents commonly have compositions with $X_{Mg} > 0.95$ ($X_{Mg} = Mg/(Fe + Mg)$). For this reason, the amount of Fe is negligible in most dolomite marbles and magnesian skarns. This fact can be seen in the chemical composition of the Loma Marcelo skarn through the Mg number ($\text{Mg}# = (100 \times \text{MgO})/(\text{FeO} + \text{MgO})$), which has values of about 98.60% in the magnesian skarn and between 24.10 and 56.89% in the calcic skarn (Supplementary Material 7). The mainly calcitic composition of the magnesian skarn matrix would be related to the consumption of dolomite during the prograde metamorphism, favouring the concentration of calcite in the matrix and the concomitant decrease in the modal content of dolomite.

Upper-crust-normalized spidergrams of skarn samples show little fractionation of incompatible elements relative to more compatible ones and negative anomalies of Rb, Ba, K, and Ni in the calcic skarn. Rb, K, and Ti behave similarly in the magnesian skarn (Fig. 13c, d). In the patterns of the two types of skarns, it can be seen that the concentration of trace elements is greater in the calcic skarn than in the magnesian skarn by approximately one order of magnitude. The total REE reaches 44.28–110.15 ppm in the calcic skarn and 10.47–28.79 ppm in the magnesian skarn (Supplementary Material 7). Chondrite-normalized REE patterns indicate enrichment of LREE ($\text{LaN}/\text{LuN} = 3.53–14.65$) and negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.33–0.85$) (Fig. 13e). Although the calcic skarn is characterized by the presence of garnet in sometimes considerable quantities, the occurrence of this mineral is not reflected in its flat to negative slopes of the HREE patterns ($\text{TbN}/\text{LuN} = 0.97–1.85$), suggesting a low content and/or little fractionation of these elements in the garnet from the Loma Marcelo skarn.

7. Geochronology

7.1. LA-ICP-MS U-Pb in zircons

The zircons separated from the calcic skarn sample 11415 are translucent, colourless to brownish, and have prismatic and subrounded shapes. Some crystals are intensely metamictized. In order to determine the internal structure of the zircon crystals, micrographs with transmitted polarized light and normal reflected light and backscattered electron images (SEM) were obtained. The analysis of the different types of images revealed oscillatory zoning, thorite inclusions, and/or xenocrystalline cores in some crystals (Fig. 14).

Twenty-three spots were analysed by LA-ICP-MS (Supplementary Material 8). When plotted on the Wetherill concordia diagram (Fig. 15a), the 23 points exhibit variable degrees of discordance and
Fig. 13. Pie diagrams of the major element composition for the calcic [(a), average of six samples] and magnesian [(b), average of three samples] skarn. Trace element diagrams normalized to upper crust values (Taylor and McLennan, 1985) for the calcic (c) and magnesian (d) skarn. e) Rare earth element diagram normalized to chondrite values (McDonough and Sun, 1995) for the Loma Marcelo skarn (the crosses correspond to the upper crust values of Taylor and McLennan (1985)).

Fig. 14. a) Zircon crystals analysed by LA-ICP-MS method (under the binocular microscope). b) Prismatic zircon crystal in calcite matrix (plane polarized light view). c) Prismatic zircon crystal with xenocrystalline core in calcite matrix (crossed Nicols view). d) Corroded zircon crystal with subrounded thorite inclusions (backscattered electron image). e) Subhedral zircon crystal with oscillatory zoning (backscattered electron image). f) Backscattered electron image of a zircon crystal included in garnet.
define a discordia line close to the concordia line. A single zircon defines an upper intercept age of 648 ± 21 Ma (MSWD = 1.5) (Fig. 15b), whereas two zircons define a lower intercept age of 353.4 ± 6.7 Ma (MSWD = 0.90) (Fig. 15c). The upper intercept age would correspond to the crystallization age of the analysed zircon, whereas the ages lower than around 600 Ma are interpreted as resulting from Pb loss due to metamorphism and deformation. The lower intercept age would correspond to the tectonothermal event responsible for such a loss.
7.2. Sm-Nd garnet-whole rock isochrons

Skarn samples 11415 and 19240 were analysed by the Sm-Nd method and two-point isochrons were constructed from the analytical results of concentrates of garnet types 1 (11415) and 2 (19240) and their corresponding whole rock (WR) samples (Supplementary Material 9). Type 3 garnet could not be concentrated because of its small grain size and lack of magnetic susceptibility. Garnets are very resistant minerals, characterized by their low REE contents and by fractionation of these elements during their formation, increasing their HREE content and conferring a higher Sm/Nd ratio (Cordani et al., 2005). It is for this reason that garnets have been widely used in the Sm-Nd isotopic dating of garnetiferous metamorphic rocks (e.g. Griffin and Brueckner, 1980; Vance and O’Nions, 1990).

The two-point isochron for the pair GrtType-1-WR11415 indicates an age of 464.0 ± 94.0 Ma with an initial 143Nd/144Nd ratio of 0.511123 ± 0.000021 (Fig. 16a), whereas the two-point isochron for the pair GrtType-2-WR19240 indicates an age of 526.8 ± 12.0 Ma with an initial 143Nd/144Nd ratio of 0.510763 ± 0.000017 (Fig. 16b). The Terreneuvian age determined for the type 2 garnet-whole rock pair coincides with the age of the Early Cambrian alkaline magmatism of the Ventania System (ca. 533–524 Ma). On the other hand, the Darriwilian age determined for the type 1 garnet-whole rock pair has no geological meaning since in the Ventania System there are no records of igneous or metamorphic activity of Ordovician age. The 464 Ma mean can be interpreted as a resetting age due to opening of the Sm-Nd isotopic system that occurred during the Early Cambrian.

7.3. Rb-Sr quartz-sericite isochron

Sample 1819 comes from a quartz ± sericite vein that post-tectonically cuts the granitic mylonites in the southern sector of Loma Marcelo. This sample was analysed by the Rb-Sr method and a two-point isochron was constructed from the analytical results of concentrates of quartz and sericite (Supplementary Material 10). The different degree of fractionation of Rb and Sr in these minerals is responsible for the higher Rb/Sr ratio of the sericite, allowing the quartz-sericite pair to be used as a geochronometer. Both elements constitute impurities in quartz, while Rb is the main substitute for K in micas.

The Rb-Sr two-point isochron indicates an age of 364.4 ± 3.6 Ma with an initial 87Sr/86Sr ratio of 0.746063 ± 0.000283 (Fig. 16c). This Famennian age is close to the Tournaisian age of 353.4 ± 6.7 Ma recorded in the Loma Marcelo skarn zircons. Using new decay constants, Varela et al. (1990) recalculated the Rb-Sr and K-Ar ages obtained by Cingolani and Varela (1973) and Varela and Cingolani (1976) in basement rocks of the Ventania System. Among the recalculated ages, an age of 360 ± 21 Ma (Rb-Sr, whole rock) was obtained for peralkaline rhyolites from Cerro La Ermita and Estancia La Mascota. Varela and Cingolani (1976) interpreted this age as a result of resetting of the isotope system.

8. Stable isotopes

Oxygen stable isotope determinations in garnet, clinopyroxene, wollastonite, vesuvianite, chondrodite, and spinel from the Loma Marcelo skarn are plotted in Fig. 17 and listed in Supplementary Material 11. The δ18O values of garnets from LM-9 and LM-13 vary between +5.1 and +8.1‰. LM-4 garnet is the most enriched (δ18O = +12.5‰), whereas LM-10 garnet is the most depleted (δ18O = −2.9‰). Clinopyroxene exhibits a wide range of δ18O values, varying from −6.6‰ (LM-9) to +9.3‰ (LM-4), as does wollastonite (δ18O = +5.8/+19.3‰). The δ18O values of vesuvianite from different outcrops are between +7.3 and +8.4‰, exhibiting very little variation. In LM-6, the values of δ18O are +11.0 and +11.5‰ for the chondrodite and +15.1‰ for the spinel.

Some of the values shown in Supplementary Material 11 are anomalous and not of primary nature, such as those from LM-10 (especially garnet and wollastonite). Clinopyroxene from LM-9 is depleted in 18O. Vesuvianite, however, presents similar values in all samples.

The wide range of δ18O values would indicate water-rock interaction processes. On the other hand, differences in absolute δ18O values suggest that the fluid nature was diverse, or that a single type of fluid interacted with the minerals, it did so under varying temperatures and water-rock ratios, among other factors.

Fig. 17. Stable isotope determinations of oxygen in silicates and oxides from the Loma Marcelo skarn. The fields of magmatic and metamorphic waters (Rollinson, 1993) are shown for comparative purposes.
e.g. the Early Cambrian alkaline magmatism (carbonate xenoliths by the intrusion. The second event (M2) is linked to intrusion of the Neoproterozoic S-type granite and the incorporation of igneous and metamorphic origin. The metasomatic events associated with the circulation of we link the genesis of the Loma Marcelo skarn to three overlapping 9.1. The Loma Marcelo skarn and its polymetamorphic history 9. Discussion 9.1. The Loma Marcelo skarn and its polymetamorphic history

On the basis of the above results integrated with previous studies, we link the genesis of the Loma Marcelo skarn to three overlapping metasomatic events associated with the circulation of fluids of both igneous and metamorphic origin. The first event (M1) is related to the intrusion of the Neoproterozoic S-type granite and the incorporation of carbonate xenoliths by the intrusion. The second event (M2) is linked to the Early Cambrian alkaline magmatism (e.g. Cerro Colorado and Estancia Agua Blanca granites). The third event (M3) is related here to a possible regional metamorphism of Late Devonian–Early Carboniferous age responsible for the mylonitization of the basement rocks of the Ventania System.

The protoliths of the Loma Marcelo skarn may have been incorporated during the intrusion of the Neoproterozoic granite (ca. 607–581 Ma; Rapela et al., 2003; Tohver et al., 2012) and metasomatized in the first instance by their magmatic fluids. This M1 event is represented by type 1 garnet, dark green clinopyroxene, wollastonite, meionite, and bytownite in the calcic skarn (Table 1). Since the skarn is included within the granite, the maximum temperature reached during the M1 event should have been about 700 °C, the temperature around which granitic magmas crystallize. In water-rich siliceous carbonate rocks and under closed system conditions, wollastonite begins to form at 600 °C and its stability field extends above 700 °C at 200 MPa (Bucher and Grapes, 2011).

The M2 event was responsible for fluorine influx into the Neoproterozoic basement, for the formation of type 2 garnet, light green clinopyroxene, and vesuvianite in the calcic skarn, and for the generation of chondrodite in the magnesian skarn (Table 1). The chondrodite would have formed by hydration of forsterite, a mineral that, together with the spinel, would have constituted the high-temperature paragenesis formed during the M1 event in the magnesian skarn. At low pressures, the humite-group minerals do not require unusual temperatures or fluid compositions to be stable in metamorphosed carbonate rocks, with the availability of F in the protolith and/or in metasomatic fluids being the most important factor determining their occurrence (Rice, 1980). The lack of forsterite in the magnesian skarn suggests its consumption during the chondrodite-generating reactions.

The high contents of F in minerals such as vesuvianite (up to 2.70% F) and chondrodite (8.69% F on average) indicate the development of F-metasomatism. The Sm-Nd age of 526.8 ± 12.0 Ma (type 2 garnet-whole rock pair) allows us to relate this second event to the post-magmatic hydrothermal activity of the Early Cambrian alkaline magmatism (ca. 533–524 Ma; Rapela et al., 2003; Tohver et al., 2012). This magmatism is characterized by A-type granites with fluorite as a common accessory mineral and F contents of up to 2.89% (Gregori, 1993). In addition, the titanite crystals from the calcic skarn show compositional zoning, with low F contents in the core and higher amounts in the rims. This F variation suggests the development of two retrogradation stages related to pre- and post-M2 events, respectively lower and higher in F. The genesis of dozyite would also be related to the retrogradation stage subsequent to the M2 event.

Gregori and Greco (1993) identified albitionization, biotitization, and fluoritization processes of post-magmatic hydrothermal origin in the Early Cambrian alkaline magmatism. According to them, albitionization and biotitization would have occurred at temperatures bracketed between 400 and 500 °C, whereas fluoritization occurred around at 320 °C. This last temperature may be applied to the F-metasomatism in the skarn.

Finally, the M3 event is represented by type 3 garnet (Table 1), interpreted as post-tectonic with respect to mylonitization. It was

---

Table 1
Paragenetic prograde sequence for the Loma Marcelo skarn.

| Event | M1* | M2* | M3* |
|-------|-----|-----|-----|
| Age (Ma) | ca. 607 | ca. 527 | ca. 364–353 |
| Garnet | ● | ● | ● |
| Clinopyroxene | ● | ● | ● |
| Wollastonite | ● | ● | ● |
| Scapolite | ● | ● | ● |
| Plagioclase | ● | ● | ● |
| Vesuvianite | ● | ● | ● |
| Calcite | ● | ● | ● |
| Forsterite (?) | ● | ● | ● |
| Spinel | ● | ● | ● |
| Chondrodite | ● | ● | ● |
| Dolomite | ● | ● | ● |
| Calcite | ● | ● | ● |

* Neoproterozoic S-type granite intrusion and contact metamorphism of carbonate xenoliths and skarn formation.
* Post-magmatic hydrothermalism related to Early Cambrian A-type magmatism and F-metasomatism of the skarn.
* Regional metamorphism and mylonitization of basement rocks.

---

Fig. 18. Temperature dependence of oxygen between an aqueous fluid and the minerals from the Loma Marcelo skarn listed in Supplementary Material 11. The fractionation factors used are those of Zheng (1991, 1993a,b).
formed by processes of static crystallization, evidenced by the lack of deformational features. The formation of almost pure grossular and the extreme mobility of elements during the mylonitization of the basement rocks of the Sauce Chico Inlier would be related to the action of fluids with fluoride complexes that increased the mobility of Al and other elements. A third retrogradation process is proposed as the one responsible for the formation of epidote in the calcic skarn and serpentine in the magnesian skarn.

The regional metamorphism related to the M3 event is assigned to the Late Devonian–Early Carboniferous on the basis of a LA-ICP-MS U-Pb lower intercept age of 353.4 ± 6.7 Ma determined on zircons of the skarn as well as a Rb-Sr quartz-sericite isochron age of 364.4 ± 3.6 Ma obtained from a quartz vein that post-tectonically cuts the already mylonitized granites. This event could be responsible for the ductile deformation evidenced in the crystalline basement and the Palaeozoic sedimentary cover. On the basis of lithofacial and structural differences between the Ventana and Pillahuincó groups, Massabie and Rossello (1984) assigned the deformation of the Ventania System to the Chanic Orogenic Phase (Late Devonian–Early Carboniferous; Turner and Méndez, 1975), in addition to the San Rafael Orogenic Phase (Early Permian). Ramos et al. (1984) related this orogeny to the collision of the Chilenia terrane with the Gondwanan margin. Tomézzoli (2012) attributed the deformation evidenced on the SW edge of Gondwana to the collision of the Patagonia and Chilenia terranes from the south and from the west, respectively; the collisions of both terranes would have begun at the same time during the Middle Devonian.

Oxygen stable isotopes in silicates and oxides from the Loma Marcelo skarn suggest extensive interaction with hydrothermal fluids of igneous, metamorphic, and possibly meteoric origin. The δ¹⁸O values expected in an aqueous fluid in equilibrium with the analysed minerals as temperature changes are shown in Fig. 18. In a δ¹⁸O-H₂O-temperature diagram, fluid values are represented by trajectories for each cogenetic mineral that should coincide at some point if the system is in equilibrium. The intersection point indicates the equilibrium temperature between the minerals and the fluid. However, as can be seen in Fig. 18, the trajectories rarely coincide, and when they do the temperatures are not geologically reasonable.

Fig. 19 shows “delta-delta” diagrams constructed for some cogenetic mineral pairs from the Loma Marcelo skarn (“a” and “b” correspond to the M1 event and “c” and “d” to the M2 event). The yellow circles correspond to the measured values and the parallel lines are the isotherms of 300 °C (blue), 500 °C (red), and 700 °C (green). Isothermal lines were calculated after Javoy et al. (1970) with the fractionation factors of Zheng (1993a,b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 20. Comparison of the stable isotope compositions between the Loma Marcelo skarn, limestones of different ages, and carbonatites from different continents (isotope data from Ballivián Justiniano et al. (2015), modified from Bell and Simonetti (2009)).
equilibrium does not exist). Thus, it is evident that the fluid activity in the basement rocks of the Sauce Chico Inlier was intense. This fluid activity could have been responsible for an effective distribution of heat and weakening of the materials, contributing to the ductile shearing observed in the crystalline basement of the Ventania System (Sellés-Martínez, 2001).

9.2. Origin of the carbonate protoliths of the Loma Marcelo skarn

Skarns are rocks formed by the interaction of carbonate and silicate systems in mutual contact (Zharikov et al., 2011). They are formed from carbonate protoliths of diverse nature, like limestones, dolostones, marls, hydrothermal carbonates, carbonatites, and marbles. Regardless of the composition of the protolith, what defines a rock as skarn is the mineralogy resulting from metasomatic alteration, which includes numerous calc-silicate or magnesian minerals, depending on the chemical composition of the protolith (Einaudi et al., 1981; Meinert, 1992). Regarding the geological environment, skarns can be formed during regional, dynamic, or contact metamorphism through metasomatic processes involving fluids of magmatic, metamorphic, meteoric, and/or marine origin (Meinert et al., 2005).

The possibility that the Loma Marcelo skarn derived from a carbonatic protolith intruded into the Sauce Chico Inlier granites was first considered due to the elongated and dyke-like arrangement of the skarn boudins, the presence of certain mineral associations and textures, and the regional petrotectonic context during the Early to Middle Cambrian (Ballivián Justiniano et al., 2015). However, the low total trace element contents and the marked negative Eu anomalies present in the Loma Marcelo skarn are features typical of carbonate protoliths of diverse nature, like limestones and marbles (Ballivián Justiniano et al., 2002).

The minimum sedimentation age is provided by the crystallization age of the analysed zircon, providing the maximum source region. The age of 648 ± 21 Ma is interpreted as the crystallization age of the S-type granite that includes the skarn (Ballivián Justiniano et al., 2015). In consequence, the sedimentation of the calcic skarn protolith should have occurred between the Late Cryogenian (post-648 Ma) and the Early Ediacaran (pre-607 Ma). In this regard, it is noteworthy that Neoproterozoic limestones are key geological features widely distributed along the Brasiliano–Pan-African orogenic belts that amalgamated old cratonic cores during the assembly of West Gondwana. Neoproterozoic sedimentary successions were largely accumulated during extensional events associated with the breakup of Rodinia in South America (Misi et al., 2007). These units consist of carbonate and siliciclastic rocks deposited in epicontinental seaways and shallow marine environments on passive cratonic margins. During the Brasiliano–Pan-African orogeny, the Neoproterozoic sedimentary sequences were deformed into mobile belts surrounding the cratons. The main South American basins of Neoproterozoic–Early Palaeozoic
The carbonate sequences of the Tandilia System (Fig. 22) are represented by dolostones of Villa Mónica Formation and limestones of Loma Negra Formation, both belonging to the Sierras Bayas Group (Dalla Salda and Iníguez Rodríguez, 1979; Poiré, 1993), underlying the siliciclastic sedimentary rocks of the Cerro Negro and Balcarce formations (Amos et al., 1972; Dalla Salda and Iníguez Rodríguez, 1979). The Villa Mónica Formation has a maximum thickness of 70 m and is composed of a lower quartz-arkosic facies and upper dolomitic and pelitic facies (Poiré and Spalletti, 2005). The dolomitic sequence consists of 36 to 52 m of stromatolitic and laminated yellowish dolostones with shales and marls and small mudstone lenses. For its part, the Loma Negra Formation consists of 40 m of reddish and black mudstones (Poiré and Spalletti, 2005). Based on C, O, and Sr isotopic data, Gómez Peral et al. (2007) assigned the ages of the carbonate
The sedimentary nature of the protoliths of both types of skarns is controlled by the dike Inlier granite. The generation of calcic and magnesian skarns was

10. Conclusions

The Loma Marcelo skarn was formed from carbonate xenoliths of sedimentary origin incorporated during the intrusion of the Sauce Chico Inlier granite. The generation of calcic and magnesian skarns was controlled by the different compositions of their carbonate protoliths. The sedimentary nature of the protoliths of both types of skarns is reflected in their chemical and mineralogical compositions. These protoliths would be genetically related to the Neoproterozoic carbonate rocks recorded in the Brasiliano–Pan-African orogenic belts of Eastern South America and Western Africa. The LA-ICP-MS U-Pb age of 648 ± 21 Ma determined in a single zircon of the skarn supports this assumption. The source area for the Loma Marcelo skarn protoliths could be the Neoproterozoic carbonate rocks from the underground of the Claromecó Basin.

The skarn is the result of the following three different metasomatic events (M) linked to fluids of igneous and metamorphic origin: M1) intrusion of the Neoproterozoic S-type granite; M2) Early Cambrian alkaline magmatism and its post-magmatic hydrothermal activity (e.g. Cerro Colorado and Estancia Agua Blanca granites); and M3) regional metamorphism of the Late Devonian–Early Carboniferous.

The Neoproterozoic age of the M1 event is given by the isotopic dating in zircons of the Sauce Chico Inlier granites that contain the Loma Marcelo skarn. Regarding the M2 event, the recognition of high-F minerals in the skarn (e.g. vesuvianite, chondrodite) and the Sm-Nd isochron age of 526.8 ± 12.0 Ma allowed the strong F-metasomatism to be associated with the Early Cambrian magmatism. The possible age of the M3 event is supported by the LA-ICP-MS U-Pb lower intercept age of 353.4 ± 6.7 Ma determined on zircons of the calcic skarn and by a Rb-Sr isochron age of 364.4 ± 3.6 Ma obtained on a vein which post-tectonically cuts the already deformed rocks.

Acknowledgements

This work constitutes part of the doctoral thesis of the first author supported by a student grant awarded by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) of Argentina. We would like to thank Pablo D. González (Universidad Nacional de Río Negro, Argentina) for helping with the U-Pb dating. We also thank Agustín Martín-Izard (Universidad de Oviedo, Spain) and Fernando Colombo (Universidad Nacional de Córdoba, Argentina) for helping with the electron microprobe. This study was supported by research grants awarded by the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC) and the Universidad Nacional de La Plata (UNLP). We warmly acknowledge the reviews by P.D. González and an anonymous reviewer, which improved the original manuscript considerably.
