Sr, C and O isotope composition of marbles from the Sierra de Ancasti, Eastern Sierras Pampeanas, Argentina: age and constraints for the Neoproterozoic–Lower Paleozoic evolution of the proto-Gondwana margin

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ABSTRACT

The Sierra Brava Complex on the eastern flank of the Sierra de Ancasti consists of marbles, metabasites, calc-silicate rocks, psammo-pelitic schists and gneisses. In the central part of this sierra a thick succession of banded schists (Ancasti Formation) crops out. Regional metamorphism of these rocks is attributed to the Famatinian orogeny (Ordovician), metamorphic grade increasing westwards and southwards and culminating in a migmatite complex on the western side of the Sierra. The meta-carbonate rocks are subdivided into a northeastern group (low-grade calcite marbles), and a southeastern group (high-grade calcite and calcite-dolomite marbles). Twenty-three marble samples were analysed for Sr isotope composition and Rb, Mn, Mg and Ca contents, and six for C and O isotope composition. An Ediacaran depositional age of 570 – 590 Ma is inferred by reference to the trend of 87Sr/86Sr in Neoproterozoic seawater. Thus the metacarbonates are probably slightly older than the Ancasti Formation (equivalent to the Puncoviscana Formation of northern Argentina), which has a maximum sedimentation age of ca. 570 Ma. Ediacaran depositional ages have also been reported for metacarbonates elsewhere in Argentina, Uruguay and Brazil. We propose that the Sierra de Ancasti carbonates on one hand, and those in the Western Sierras Pampeanas (Difunta Correa Sequence) and -tentatively- the Corumbá Group of Brazil on the other, represent platforms on opposite margins of the extinct Clymene Ocean, whereas Neoproterozoic carbonate successions such as the Loma Negra Formation (Tandilia, southern Argentina) and the Arroyo del Soldado Group (Uruguay) were deposited on the eastern side (present coordinates) of the Río de la Plata craton, which at the time occupied a position farther to the north.

INTRODUCTION

The Sierras Pampeanas of Argentina represent the foreland of the Andean orogen. Most sierras occur from 24 to 34°S, and 63 to 70°W, coinciding with the present-day flat-slab sector of the Nazca Plate. The Sierras Pampeanas are subdivided into two main sectors. The Western Sierras Pampeanas (WSP, Fig. 1A) are formed by a Grenville-age complex (1000 - 1250Ma) of meta-igneous and metasedimentary rocks (Vujovich et al., 2004; Casquet et al. 2004; 2008a) that was episodically intruded by A-type granites and carbonatite-syenite during the Neoproterozoic (Baldo et al., 2008; Casquet et al., 2008b; Colombo et al., 2009). This complex was the basement to a late-Neoproterozoic sedimentary sequence with siliciclastic and carbonate deposits, i.e., the Difunta Correa Sedimentary sequence (Casquet et al., 2001). Both basement and cover were further involved in deformation and metamorphism in the Middle Ordovician (Casquet et al., 2001; Varela et al., 2001; Galindo et al., 2004; Rapela et al., 2005). The Eastern Sierras Pampeanas (ESP, Fig. 1A) consist of a low-to high-grade metasedimentary complex and plutonic units emplaced in the Early Cambrian, Middle Ordovician and Upper Devonian to Lower Carboniferous (Sims et al., 1998; Rapela et al., 1998; 2007; Dahlquist et al., 2008). The main tectono-thermal event in this sector -metamorphism and
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The Sierra de Ancasti, in Catamarca province, lies at the eastern edge of the ESP (Fig. 1A) and is mainly composed of metamorphic and plutonic rocks; the excellent quality of the outcrops makes this Sierra a good place for investigating the sedimentary, magmatic and tectothermal evolution of the pre-Andean basement. Similar rocks extend northward into the Sierra del Aconcagua, whilst to the south and east they disappear under the Cenozoic cover.

The eastern and southern parts of the Sierra de Ancasti consist of metasedimentary successions (quartz-mica schists, Ca and Ca-Mg marbles, quartzite, biotite-gneisses and metabasites) known as the Sierra Brava Complex (Aceñolaza et al., 1983). The central part of the Sierra is formed by a thick succession of banded schists, and minor calc-silicate rock of the Ancasti Formation (Willner, 1983). Marbles are lacking in the central sector. The western side consists of gneisses and migmatites of the El Portezuelo Formation (Aceñolaza et al., 1983); this is the highest-grade metamorphic unit. Granitic to granodioritic intrusions of a few kilometers in size are found throughout the sierra, and pegmatite dykes and sills are locally found near the limit with the El Portezuelo Formation. Recently, Rapela et al. (2007) using U-Pb SHRIMP zircon dating constrained the age of sedimentation of the Ancasti Formation to a maximum of 570 Ma, and found ages of 466 ± 5 to 471 ± 5 Ma for two of the granitic intrusions.

The sedimentary protoliths of the ESP were formerly correlated with the Late Neoproterozoic to Early Cambrian Puncoviscana Formation (Rapela et al., 1998, 2007; Schwartz and Gromet, 2004; Toselli et al., 2005). The latter is a remarkable sedimentary sequence that extends from Bolivia to Central Argentina. It consists largely of a thick turbidite-pelite-greywacke sequence with locally interbedded conglomerates, shelf limestones and volcanic rocks (for reviews see: Omarini et al., 1999; Do Campo and Guevara, 2005; Zimmermann, 2005; Adams et al., 2008). The Sr, C and O isotopic signature of carbonates from the Puncoviscana Formation was interpreted to correspond to the Neoproterozoic-Cambrian transition (Sial et al., 2001). Age constraints from trace fossils, K/Ar geochronology, some granitic intrusions and inherited detrital zircon dating (Schwartz and Gromet, 2004; Toselli et al., 2005; Adams et al., 2008) all point in the same direction.

Evidence from fossils is lacking in the metacarbonate rocks of ESP, so that the isotopic ratios of Sr, C and O remain the best way to constrain the age of sedimentation and to establish regional correlations. In this contribution an Ediacaran age for the marbles from the Sierra Brava Complex of the Sierra de Ancasti is inferred from Sr, C and O isotopic ratios of the carbonate fraction of marbles. Moreover, the Ancasti marbles can be correlated with metacarbonates elsewhere including those in WSP, the Puncoviscana Formation and carbonate outcrops of similar ages located along the western margin of Gondwana, permitting us to postulate the coeval existence of different basins in the Ediacaran.

**SAMPLEING AND ANALYTICAL METHODS**

Thirty-one samples of marbles were collected at both low- and high-grade locations of the Sierra de Ancasti. Thin sections of all the samples were firstly stained for carbonates and then studied under the microscope. Geographical locations, descriptions and mineral compositions of the samples are shown in Table 1.

All the samples were analysed for Sr isotope composition at the Geochronology and Isotope Geochemistry Centre of Madrid University, and six samples were chosen for C and O isotope composition. The carbonate fractions of most samples were analysed for Mn, Mg, Sr and Ca to evaluate the degree of post-sedimentary alteration (geochemical screening). To exclude contamination from other minerals, carbonate samples (~ 30 mg) were leached in a 10 % acetic acid solution and then centrifuged to remove the insoluble residua (Fuenlabrada and Galindo, 2001). The solution was subsequently evaporated and then dissolved in 3 ml of 2.5N HCl. Sr was separated using cation-exchange columns filled with BioRad® 50W X12 (200/400 mesh) resin. Procedural blank was less than 2ng for Sr. The Sr isotope composition was determined on an automated multicollector SECTOR 54® mass spectrometer and the results are displayed in Table 2. 87Sr/86Sr values were normalized to an 87Sr/86Sr value of 0.1194. The NBS-987 standard was routinely analysed along with our samples and gave an average 87Sr/86Sr value of 0.710251 ± 0.000002 (2σ, n=7). Individual precision estimates (standard error on the mean) are given in Table 2; overall analytical uncertainty is estimated to be ± 0.01%. The Rb and Sr contents included in Table 2 were determined on unleached whole-rock powders (by ICP-MS and ICP-OES respectively) and hence include the effects of any minor contaminants to the carbonates. Thus no age-corrections were considered necessary for the 87Sr/86Sr ratios determined on leachates, which should not include any Rb-enriched phases (although it may be noted that even using the whole-rock Rb/Sr ratios, such corrections would be less than 0.0003 for the majority of samples, even where there is independent evidence of alteration). Oxygen and C isotope determinations were carried out on a double inlet Micromass SIRA-II® mass spectrometer at

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**TABLE 1**

<table>
<thead>
<tr>
<th>Location</th>
<th>Description</th>
<th>Mineral Composition</th>
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<tbody>
<tr>
<td>Sierra Brava Complex</td>
<td>High-grade location</td>
<td>gneisses, migmatites</td>
</tr>
<tr>
<td>El Portezuelo Formation</td>
<td>Low-grade location</td>
<td>schists, quartzite</td>
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</table>

**TABLE 2**

<table>
<thead>
<tr>
<th>Location</th>
<th>Rb含量 (mg/g)</th>
<th>Sr含量 (mg/g)</th>
<th>87Sr/86Sr</th>
<th>86Sr值 (‰)</th>
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</thead>
<tbody>
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<td>Sierra Brava Complex</td>
<td>High-grade location</td>
<td>3.25</td>
<td>75.6</td>
<td>0.710251 ± 0.000002</td>
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<tr>
<td>El Portezuelo Formation</td>
<td>Low-grade location</td>
<td>3.50</td>
<td>72.7</td>
<td>0.710249 ± 0.000002</td>
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</tbody>
</table>

---

**Notes:**
- **Rb** and **Sr** were determined on unleached whole-rock powders (by ICP-MS and ICP-OES respectively).
- **Sr** ratios were normalized to a **87Sr/86Sr** value of 0.1194.
- **NBS-987** standard was routinely analysed along with our samples.
- **Overall analytical uncertainty** is estimated to be ± 0.01%.
Sr, C and O isotope composition of marbles from the Sierra de Ancasti, Argentina

THE MARBLES OF ANCASTI

Field relations, Petrography and isotope composition

The main outcrops of marbles are found along the northeastern side of the Sierra; some of these are currently quarried for cement. The larger quarries (La Calera, Ancajan and Albigasta, Fig. 1B, coordinates in Table 1) exploit C-marmoles (Ca ~ 38 to 51%; mean ≈ 47% (n = 15), Table 2). A second group of quarries is in the south and southeast of the Sierra (La Montosa, Hermanos Moya, La Escondida and El Cerrito quarries), exploited marble ranging from Ca to Ca-Mg-type (Ca ~ 31 to 51%; mean ≈ 38% (n = 8), Table 2).

Marbles in the northeast underwent low- to medium-grade regional metamorphism. The assemblage: Cal (± Ms ± Phl ± Qtz) with ± Gr and ± Py as accessories (abbreviations after Siivola and Schmid, 2007) is common in the marble. The assemblages Ms + Bt + Chl + Grt and Am + Ep + Chl + Pl are found in meta-psammites and meta-basic schist respectively, associated with marbles. On the other hand, metacarbonates from the south to southeast record medium- and high-grade metamorphic conditions as suggested by the mineral associations Cal (± Ms ± Qtz ± Tr) and Cal - Dol - Fo (± Spl ± Clc ± Tr), in Ca and Ca-Mg marbles respectively. The assemblage Sil + Bt is found in the associated paragneisses and migmatites.

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<table>
<thead>
<tr>
<th>Sample</th>
<th>latitude</th>
<th>longitude</th>
<th>Location</th>
<th>Rock description</th>
<th>% Acc. [IR %]</th>
<th>Mineralogy (mineral abbreviation after Siivola and Schmid, 2007)</th>
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<td>ANC-10108</td>
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<td>63°15′14.4″</td>
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<td>Cal - Qtz - Gr - opaque minerals - Py - Ms - Phl - CHN</td>
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<td>massive grey marble</td>
<td>4 - 7 [12.88]</td>
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<td>65°15′04.6″</td>
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<td>Cal - Qtz - Ms - (Phl - Gr - opaque minerals - Pl)</td>
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<td>18 - 21</td>
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<td>massive pink marble</td>
<td>1 - 2</td>
<td>Cal - Dol - Tr - (Qtz)</td>
<td></td>
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Table 1. Location, field description and petrography of marbles. *Not analyzed for geochemistry. [IR %]: insoluble residue
Northeast Sector

In La Calera (Fig. 1B), the metacarbonates, quartzite, quartz-micaceous schist, quartz-carbonate schist and amphibolites form a folded succession of SE–NW strikes, dipping 20 to 40º SW (Fig. 2A-B and 3A). In the La Calera quarry these constitute the northern flank of an antiformal fold (Willner, 1983, Fig. 2A-B).

The predominant marbles are massive, white in colour, and alternate with a banded type (centimetric bands of white and grey marble). These are fine- to medium-grained metacarbonates (Fig. 3A-B), composed of Cal ± (Phl - Qtz - Gr - Py - Ms - Pl - Chl - opaque minerals). The texture is fine granoblastic, with an average grain-size of 0.5mm (Fig. 4C). Patches of porphyroclastic texture are linked to ductile deformation, with a thin granoblastic matrix around calcite porphyroclasts (Fig. 4D). Quartz veinlets of a few millimetres up to 2cm wide are present in specific sectors (Fig. 4B). Sulphides, mostly pyrite (Fig. 4E), are scarce and restricted to certain levels.

In this sector, 11 representative samples of the three principal levels of marbles were analysed (Fig. 4). All are calcic-marbles, with an average composition of Ca = 46.6% and Mg = 0.36%, Sr = 1577ppm, Rb = 12.3ppm and Mn
between 29 and 622 ppm (Table 2). Only three of the eleven have Mn/Sr and Mg/Ca ratios that suggest significant post-sedimentary changes according to the criteria of Melezhik et al. (2001) (Table 2 and Fig. 5A and B).

The \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios of these samples fall into two groups, five samples with 0.70831 – 0.70860, and six samples with 0.70747 – 0.70781 (Table 2, Fig. 5C). The latter group presents the lowest alteration indices, and low percentages of accessory minerals (except sample ANC-11006, which has 17 – 20 % modal of accessories, essentially quartz). Figure 3 shows the distributions of \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios of these samples arranged stratigraphically. Variations do not seem to correlate with stratigraphic position. C- and O-isotope compositions were determined in two samples from this sector with the lowest grade alteration, and a third which was only slightly more altered. All three have very similar values of C and O (δ\(^{13}\text{C}\)PDB ~ +8.36 to +9.05‰; δ\(^{18}\text{O}\)SMOW ~ +19.37 to +22.23‰, Table 2).

In the area of the Ancaján quarry (Fig. 1B), marbles with intercalations of amphibolites and schists are folded. The marbles are white to light grey in colour and show a medium-grained granoblastic texture (1 to 2 mm). The mineralogy consists of Cal + Qtz ± (Ms - opaque minerals - Zrn). The two samples of the Ancaján marbles have uniform \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios (0.70787 and 0.70769, Table 2). Both samples have a 5 to 11 % modal...
content of non-carbonate minerals, mostly quartz and to much lesser extent muscovite. The Mg/Ca and Mn/Sr ratios are well below the values that might suggest significant alteration of their primitive geochemical features (Fig. 5A-B). The O-isotope values are similar to those of the samples from La Calera ($\delta^{18}$O$_{SMOW} \sim +17.98$‰), while the C-isotope values are markedly lower ($\delta^{13}$C$_{PDB} \sim +2.96$‰, Table 2).

The marble of the Albigasta quarry, to the south of the eponymous town (Fig. 1B), forms an important subhorizontal level about 20 – 25m wide, intercalated with biotite-gneisses, amphibolites and schist. The mineral association is Cal ± (Ms - Phl - opaque minerals - Qtz). The metacarbonates have a granoblastic texture and are medium- to fine-grained (0.5 – 1mm). Mica-rich bands (Ms + Phl) of 1mm are observed, which also contain quartz and opaque minerals in smaller quantities (Fig. 6A). Two samples from this sector show very different values of $^{87}$Sr/$^{86}$Sr (0.70759 and 0.70853, Table 2). Both samples are uniform, unbanded calcic-marble (Mg/Ca = 0.006 – 0.008), but with different accessory minerals content; the sample with 0.70759 has a very low percentage of accessories (< 4 % modal). The Mn/Sr ratio is high (0.86 – 1.09) in both samples (Table 2, Fig. 5A-B).

**Southern Sector**

In the La Montosa quarry (Fig. 1B) the marbles strike 280º/70º N and alternate with biotite-gneisses, migmatites and amphibolites. They are intruded by a tonalite dyke, and a metasomatic skarn 10 to 50cm thick is developed at the contact, with the generation of coarse epidote and garnet (2 – 5cm). The white to light grey La Montosa marbles have a granoblastic texture, medium- to coarse-grained (3 – 8mm), and the main mineral association is Cal ± Dol ± Qtz ± Ms ± Chl ± Tr). Another type is a banded, light grey to dark marble, but is less abundant; it shows a more complex mineral association of Cal - Fo - Dol - Clc (± Chn ± Spl ± Srp ± Qtz, Fig. 6B-C).

The samples from this sector show contrasting values of the $^{87}$Sr/$^{86}$Sr ratio (0.70748 - 0.70867, Table 2). All samples are the massive type marble, two of them with low
percentages of accessory minerals (3 – 5% modal), low Mg/Ca ratios (0.008 – 0.009) and low Mn/Sr (0.03 – 0.15), while the third sample presents a higher accessory mineral content (16% modal) and higher Mg/Ca (0.014, Table 2).

C-isotope data for two samples from this sector show much lower values than the marbles of the northern sector (δ13C PDB ~ +0.13 to +0.97‰, Table 2), whereas the O-isotope values are only slightly lower (δ 18O SMOW ~ +16.18 to +17.25‰, Table 2).

The marbles from the Hermanos Moya and La Escondida quarries (Fig. 1B) occur within a folded succession of marbles and gneisses with minor lenses of amphibolites, observed mainly in the marble-gneiss contact. In the La Escondida quarry medium- to fine-grained biotite-muscovite granite is also present. In both quarries the marbles are medium to coarse-grained, with granoblastic textures, and in Hermanos Moya, very rich in accessory minerals (~ 20 to 30% modal of silicates, Fig. 5D-E). The mineral association in Hermanos Moya quarry is Cal - Dol - Fo (± Clc ± Spl ± Ms ± Phl ± opaque minerals ± Tr ± Srp).

One sample from the Hermanos Moya quarry shows a value of 87Sr/86Sr of 0.70844; this sample is a massive marble with 15 – 17% modal accessory minerals. Dolomite and forsterite have been detected as accessory minerals, which is also evidenced by the high Mg/Ca ratio (0.27), while the Mn/Sr ratio is low (0.13) (Table 2, Fig. 5A-B).

The sample from the La Escondida quarry is massive with very low accessory mineral content (1 – 2% modal) and has an 87Sr/86Sr of 0.70745 ratio; it has low Mn/Sr (0.08), but the Mg/Ca ratio is high (0.32), indicating the presence of dolomite (Table 2, Fig. 5A-B).

The El Cerrito quarry (now in operation) is located at the southeast end of the Sierra de Ancasti (Fig. 1B). The main marble outcrop forms a continuous body that is 90-100m thick (208º/60º E), intercalated in quartz mica-schist. This is a white to pink and light gray massive marble with coarse grain-size (2 - 5mm) and granoblastic texture. All the marbles have very low accessory minerals contents (1 - 5% modal, Fig. 6F), tremolite and quartz being the main ones. Two of the samples analyzed from this sector have 87Sr/86Sr ratios of 0.70712 and 0.70753; a third sample has a highly anomalous value compared to the rest in this study (0.71571). The Mg/Ca and Mn/Sr ratios in all cases are above the limits suggested for unchanged rocks (Table 2, Fig. 5A-B).

**DISCUSSION**

**Interpretation of chemical and isotopic values**

Metacarbonates of the northern area (La Calera, Ancajan and Albigasta quarries) and the La Montosa quarry in the southern sector, are low in MgO (less than 1%, Table 2) and mostly have very low Mg/Ca ratios (< 0.02, Table 2,

Fig. 5A-B), indicating that calcite is practically the only carbonate present. Furthermore, modal impurities in these samples (silicate and other non-carbonate accessory minerals) amount to only 5 to 15%, and the insoluble residue of a set of representative samples of this sector is less than 5% by weight. The main accessory minerals are quartz, muscovite, ore minerals, tremolite and graphite (Table 1). However, the Mg/Ca ratio is markedly increased (0.27 – 0.32) in samples from the Hermanos Moya, La Escondida and El Cerrito quarries in the south of the range, indicating the presence of a significant percentage of dolomite and Mg-rich accessory minerals in the metacarbonates.

The usefulness of the isotopic compositions of Sr, C and O strongly depends on the preservation by the carbonates of the composition in equilibrium with seawater at the time of formation. Post-depositional processes such as diagenesis and metamorphism could disturb the calculated initial compositions, invalidating their utility for isotope stratigraphy. Such processes tend to impoverish the carbonate rocks in Sr, and enrich them in Mn, and consequently Mg/Ca and Mn/Sr ratios are the main indicators of post-sedimentary experience by these rocks. According to Melezhik et al. (2001), values of Mn/Sr > 0.2 and Mg/Ca > 0.01 are indicative of secondary changes, and it is therefore recommended not to use samples that have values above these limits. It is important to consider both parameters, as post-sedimentary alteration may manifest itself in only one. Figures 5A and B show that the majority of samples tested have values below these limits, and therefore the original isotopic relations should be valid for stratigraphic correlation. The samples with low Mg/Ca and Mn/Sr ratios are also rich in Sr content (Sr between 1400 and 3600ppm) suggesting that these represent the original composition of the marine carbonates. By contrast, samples with relatively low Sr contents and higher ratios of Mg/Ca and Mn/Sr are likely to have experienced modification of initial isotopic ratios, such as those from the El Cerrito quarry (Sr 85 –114ppm, Mg/Ca > 0.04 – 0.31 and Mn/Sr > 0.22 - 0.44, Table 2, Fig. 5A-B).

Although a high proportion of the samples have Mn/Sr and Mg/Ca ratios within acceptable values, their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are not uniform. Figures 5A, 5B and 5C show a group of thirteen samples with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.70745 and 0.70787, and another group of eight samples with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.70831 and 0.70867. Most samples in the latter group fail the geochemical screening for unaltered composition, and thus their Sr isotopes probably represent significant post-sedimentary alteration. Only two samples in this group (ANC-11005 and 11007) show acceptable values for the Mn/Sr and Mg/Ca ratios and low content of accessory minerals (Tables 1 and 2). The sample ANC-11055 is similar but the Sr content is relative low (584ppm) suggesting a probable a post-sedimentary perturbation.

Age of Sierra de Ancasti carbonates and correlations

The secular variations of Sr, C and O isotopic compositions for global seawater are now established with sufficient precision to make the isotope stratigraphy of the marine carbonates possible (Veizer et al., 1999; Jacobsen and Kaufman, 1999; Montañez et al., 2000; Melezhik et al., 2001; Jiang et al., 2007; Prokoph et al., 2008). The principal condition is that the sedimentary rocks retain the isotopic ratios that they had at the time of deposition in equilibrium with sea water. The methodology is particularly useful for periods of sedimentation where the fossil evidence is scarce or lacking, such as those of marine sediments prior to the Cambrian biological explosion. Variations in the isotopic ratios of $^{87}\text{Sr}/^{86}\text{Sr}$ and C in carbonate rocks are the most commonly used, while the use of oxygen isotopes is less so because the latter are more easily affected by interaction with meteoric water and interstitial fluids at low to high temperature (Fairchild et al., 1990).

Despite the relatively high mobility of Sr and C in carbonates during diagenesis and metamorphism, under special conditions such as low fluid-rock ratios and low siliciclastic contents, these rocks can behave as nearly closed systems for the two elements, even under medium- and high-grade metamorphic conditions (Brand and Veizer, 1980; Melezhik et al., 2001).

Figure 7 shows the secular Sr isotope curve from Late Proterozoic to Lower Devonian (based on Asmerom et al., 1991; Jacobsen and Kaufman, 1999; Veizer et al., 1999, and Brasier and Shields, 2000), and also the variations of C from Proterozoic to Upper Cambrian (Jacobsen and Kaufman, 1999).

After chemical screening, two populations of samples with different values of $^{87}\text{Sr}/^{86}\text{Sr}$ were found in the Sierra de Ancasti (Table 2, Fig. 5C). Marbles with $^{87}\text{Sr}/^{86}\text{Sr}$ values between 0.70839 and 0.70867 (n = 3) intercept the secular Sr isotope curve during the Cambrian (Fig. 7). On the other hand, the group of $^{87}\text{Sr}/^{86}\text{Sr}$ values between 0.70745 and 0.70787 (n = 7) intercepts the secular curve in the Ediacaran, between ca. 570 and 590Ma. As noted above, the lowest values of ca. 0.7075 in particular are predominantly shown by low-grade samples from La Calera quarry which have very high Sr content and unmeasurable Rb, as well as low Mg/Ca ratios; 0.7075 is below any seawater values seen during the Paleozoic (see Fig. 7), so no significant subsequent equilibration can have occurred. We take these as primary values and indicative of Ediacaran deposition; the spread of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for unaltered samples up to ca. 0.7078 may indicate extended deposition during
Ediacaran times. Values of δ¹³C are only available for the low ⁸⁷Sr/⁸⁶Sr carbonates and differences apparently exist between those in the north (+2.96 to +9.05‰) and those in the south (+0.13 and +0.97‰). The heavy C isotope composition particularly of the northern samples is a good indication for isotope excursions of marine C after glaciations because of increasing productivity in the oceans (e.g., Hoefs, 1997). In fact, the Sr isotope age inferred here for the Sierra de Ancasti carbonates is broadly coincident with the period between two glaciations, the Marinoan and Moelv, which took place between 635 and 560Ma (e.g., Jacobsen and Kauffman, 1999; Brasier and Shields, 2000). From the data above, we conclude that the Sierra de Ancasti carbonates are for the most part Ediacaran. The existence of carbonates of Cambrian age cannot be disregarded on the basis of isotope composition alone. However, the fact that carbonates with relatively high ⁸⁷Sr/⁸⁶Sr values are found at the same locations as the Ediacaran carbonates suggests that they are probably coeval but underwent post-sedimentary alteration.

U-Pb SHRIMP ages of detrital zircons from the Ancasti Formation place the maximum age of sedimentation at ca. 570Ma (Rapela et al., 2007). The minimum age can be set at ca. 550Ma, i.e., when the Pampean magmatic arc started to the east (Schwartz et al., 2008). In consequence the Ancasti Formation is probably younger than the La Calera Member of the Sierra Brava Complex (570-590Ma). The Ancasti Formation shows patterns of U-Pb detrital zircon ages similar to those of other clastic metasedimentary successions in the Eastern Sierras Pampeanas (Rapela et al., 2005 and references therein) that are accordingly considered equivalent to the Puncoviscana Formation (e.g., Zimmermann, 2005).

Other metacarbonate rocks in the Sierras Pampeanas show Sr isotope compositions similar to those of the Sierra de Ancasti metacarbonates (Fig. 7). It may be concluded that all are Ediacaran in age and may thus be correlated. However, limestones of the Las Tienditas Formation located in the upper part of the Puncoviscana Formation,
show $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios higher than those of the Sierra de Ancasti metacarbonates (Omarini et al., 1999; Sial et al., 2001), suggesting a younger age of sedimentation, in agreement with maximum sedimentation ages for the Puncoviscana Formation inferred from detrital zircon ages. Moreover, these rocks underwent post-sedimentary alteration as suggested by the often high Mg/Ca and Mn/Sr ratios (Sial et al., 2001).

Fig. 8A-B shows the distribution and Sr isotope composition for the different Neoproterozoic to Early Paleozoic carbonate basins of Western Gondwana in southern South America. The metacarbonates of the Sierra de Ancasti show $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that approach those of carbonates of the Loma Negra Formation (Sierras Bayas Group of Tandilia system), Arroyo del Soldado Group (Uruguay), and the Puga Hill Formation of the Corumbá Group (Brazil) (Misi et al., 2007 and references therein). The first two lie on the Rio de la Plata Paleoproterozoic basement, whilst the third was deposited along the southeastern margin of the Amazonian craton and is apparently younger on a paleontological basis (Misi et al., 2007). In the WSP, Sr isotope compositions similar those of the Sierra de Ancasti metacarbonates are also found in
metacarbonates of the Difunta Correa Sequence (Galindo et al., 2004), and metacarbonates of the Sierra de Umango (Varela et al., 2001) (Fig. 8A-B).

Rapela et al. (2007) recently proposed a paleogeographic model of Southwestern Gondwana for the Neoproterozoic-Middle Cambrian. In this model the marine Puncoviscana basin laid down on the eastern (present coordinates) margin of the Clymene Ocean (Trindade et al., 2006), and received sedimentary input essentially through erosion of both the Mesoproterozoic Natal – Namaqua terranes along the southern Kalahari craton, and the recently emerged orogens of ca. 600Ma (Brasiliano-Panafrikan and East Africa-Antarctic orogens). The latter interpretation was inferred because of the absence of detrital zircons derived from the present nearby Río de La Plata craton on one hand, and, the evidence for significant right-lateral transpressional deformation during the collisional Early Cambrian Pampean orogeny on the other (Rapela et al., 2007). However, the size of the Clymene ocean remains a matter of debate (e.g., Cordani et al., 2009). It was further argued that the Mesoproterozoic cratonic blocks of Amazonia - Arequipa - Antofalla and the Western Sierras Pampeanas constituted a single continental mass to the west of the Clymene Ocean (Rapela et al., 2007; Casquet et al., 2008b). According to this paleogeographic interpretation, the contemporary clastic and carbonate deposits of the Eastern and Western Sierras Pampeanas do not necessarily correspond to a unique marine basin. The Difunta Correa Sequence carbonates that were deposited on the Mesoproterozoic basement of the WSP represent sedimentation on the western shelf of the Clymene Ocean (current coordinates). The Corumbá Formation of southern Brazil (Misi et al., 2007 and references therein) may correlate in part with the Difunta Correa Sequence (Sr and C isotope similarities and dissimilarities exist among the two formations) as it was also laid down along the southeastern margin of the Amazonian craton, i.e., on the western margin of the Clymene Ocean (Trindade et al., 2006). In contrast, the Sierra de Ancasti carbonates formed in a sedimentary basin on the conjugate and contemporary eastern margin of the same ocean (Fig. 9). The carbonate sedimentary successions on the Río de la Plata craton, i.e., the Sierra Bayas and Arroyo del Soldado groups were almost coeval but were laid down in epicontinental basins not related to the Clymene Ocean.

ACKNOWLEDGMENTS

This work is a contribution to Argentine projects PICT-07-10735 ANPCyT, SECyT-UNC and PIP-5719 CONICET, and Spanish grants CGL2005-02065/BTE (MEC), CGL2009-07984/BTE and GR58/08 (2009), UCM. Critical comments by Umberto G. Cordani, Colombo Tassinari and the journal editor enabled us to greatly improve the manuscript.

REFERENCES


Sr, C and O isotope composition of marbles from the Sierra de Ancasti, Argentina


Manuscript received September 2009; revision accepted March 2010; published Online December 2010.