Isotopic characterization of Jurassic evaporites. Aconcagua-Neuquén Basin, Argentina

G.L. LO FORTE \textsuperscript{11} F. ORTI \textsuperscript{21} and L. ROSELL \textsuperscript{21}

\textsuperscript{11} UB-CONICET, Departamento de Ciencias Geológicas, Facultad de Ciencias Exactas y Naturales, Pabellón II, Ciudad Universitaria, 1428 Ciudad Autónoma de Buenos Aires, Argentina. E-mail: galof@gf.fcen.uba.ar

\textsuperscript{21} Departament de Geocquímica, Petrologia i Prospecció Geològica, Universitat de Barcelona, Zona Universitaria de Pedralbes, 08028 Barcelona, Spain. Orti E-mail: f.orti@ub.edu  Rosell E-mail: lrosell@ub.edu

ABSTRACT

Isotopic analysis can be used to interpret the origin of evaporitic sediments. A preliminary isotopic study of strontium, oxygen and sulphur has been carried out in Ca-sulphate facies of Jurassic marine evaporites (Tábanos Formation and Auquilco Formation) outcropping in southern Mendoza, Aconcagua-Neuquén Basin (Argentina), as a part of a comprehensive sedimentologic study. The analysed sections are located at arroyo Las Leñitas, Cañada Ancha and arroyo Blanco. Sampled units include laminated, banded, and nodular lithofacies, made up of anhydrite, secondary gypsum and calcite. The mineralogy was studied by conventional petrographic analysis and X-ray diffraction. The $\delta^{78}Sr/\delta^{86}Sr$ ratio was obtained in six samples, with values ranging from 0.706793 to 0.706839, which match marine calcium-sulphate data of the same age. A similar conclusion may be derived from ten samples analysed for oxygen ($\delta^{18}O$) and sulphur ($\delta^{34}S$) isotopic composition: the obtained values are between $+11.55\%_e$ and $+14.42\%_e$, and between $+17.25\%_e$ and $+18.48\%_e$ respectively. The sedimentologic-stratigraphic evidence and the isotopic data both suggest a marine origin for the Tábanos and Auquilco evaporites, without an analytically detectable contribution of continental waters or hydrothermal solutions. The results also suggest that no isotope fractionation occurred during the primary gypsum-to-anhydrite-to-secondary gypsum transformations.

INTRODUCTION

Stable isotope geochemistry applied to evaporitic sediments may provide specific information about depositional and diagenetic conditions. Due to the large variability of environmental parameters (such as salinity, temperature, pH, Eh, etc.), common early diagenetic reactions (by the action of either allochthonous solutions or in situ bacterial activity), and rock-solution interactions during later diagenesis, the study of stable isotopes is essential to properly interpret the sedimentary history of evaporite sediments.

The sedimentary infilling of the Aconcagua-Neuquén Basin (West-central Argentina, Mendoza province) is well known due to academic and industry research carried out...
since the end of the 19th century. However, the detailed sedimentologic features of the evaporitic units, mainly represented by Ca-sulphates (anhydrite and secondary gypsum) and subordinate Na-chloride, are largely unknown. At present, there is some isotopic data on CaSO₄ samples from quarries located in the southern part of the basin (Brodtkorb et al., 1997, and references herein; Zappettini, 1999), in south Mendoza and Neuquén provinces. Recently, new results from outcrops and quarries located in southern Mendoza were presented by Lo Forte et al. (2003), and shortly after by Linares et al. (2003).

A preliminary isotopic study of strontium, oxygen, and sulphur was carried out on the Ca-sulphate evaporites of the marine Jurassic sequences cropping out in the Aconcagua-Neuquén Basin (Fig. 1). The aim of this paper is to characterize and discuss the isotopic composition of these sulphate deposits, as a part of a larger sedimentologic and stratigraphic study on the palaeogeographic evolution of these sequences.

**GEOLOGICAL SETTING**

Since Early Jurassic times the geodynamic evolution of the western border of southern South America has been closely related to an east-deepening subduction zone with variable rates of convergence and segmentation along latitude (Mpodozis and Ramos, 1989; Ramos, 1992). In this context, the Aconcagua-Neuquén Basin represents a back-arc depocenter generated by pericratonic extensional processes which started during the Middle Triassic (Ramos, 1992; Manceda and Figueroa, 1995) due to the fragmentation of Gondwanaland (Uliana et al., 1989). The Jurassic evaporative sequences were deposited during a thermal decay episode representing a broad epeiric sag, after a synrift event (Manceda and Figueroa, 1995).

The sediments of the Aconcagua-Neuquén Basin are siliciclastic, volcanioclastic, carbonatic and evaporitic deposits, up to 7000 metres in thickness. They are assigned to nine mesosequences controlled by tectonoestratic sea level changes ranging from Triassic to Cenozoic (Legarreta and Uliana, 1996). During Late Jurassic the sedimentary accumulation was influenced by important changes in the average position of the shoreline and the main depositional trends were driven by early-middle Callovian emergence, late Callovian to early Oxfordian flooding, and late Oxfordian to early Kimmeridgian basin shallowing and desiccation (Legarreta, 1991; Legarreta and Uliana, 1996). The stratigraphic framework of the basin during Late Jurassic in Malargüe area is briefly summarised in Figure 2.

The Tábanos and Auquilco formations are basin-filling evaporitic deposits (up to 80 and 400 metres respectively) that cover an extended area of hundred of kilometres across the basin (for detailed palaeogeography see Legarreta and Uliana, 1996). They are transgressive...
deposits of a preexisting carbonate-platform palaeotopography (Calabozo Formation and La Manga Formation and equivalents, respectively; Legarreta, 1991; Legarreta and Uliana, 1996). The basal Tábanos evaporite is palaeogeographically confined to the Calabozo slope and basinal domains revealing that the onset of sulphate deposition occurred within an almost completely desiccated basin. The evaporite beds onlap the Calabozo carbonates and locally overstep older Callovian strata. These deposits represent a transgressive event under negative hydrologic balance (Legarreta, 1991; Legarreta and Uliana, 1996). The older Auquilco evaporite is areally confined to the depositional basin of the older Oxfordian carbonates (La Manga Formation) revealing a base level fall of at least 150 m. These strata reflect an aggradational system that filled the deeper part of the desiccated basin, lapping on the former slope front. The younger Auquilco evaporite strata expanded updip just beyond the proximal edge of the Oxfordian La Manga carbonate wedge (Legarreta, 1991; Legarreta and Uliana, 1996). In several of the sampled profiles herein, the sudden transition from normal marine to hypersaline conditions is documented by shallow subtidal to intertidal carbonates and evaporites overlying hemipelagic sediments, as previously stated by Legarreta and Uliana (1996). The end of both evaporitic episodes resulted from a major base level fall, evidenced by erosional incisions, that led to the establishment of an arid to fluvial environment; the subsequent fluvial to eolian deposits are assigned to the lower Lotena Formation (and equivalent units) and Tordillo Formation (and equivalent units), respectively.

By the end of the Eocene and during the Middle Miocene a fold-thrust belt was developed, which produced the present structure of the basin. This fold and thrust belt is characterized by a series of east-verging folds and related thrusts, which developed a complex thrust front with duplexes and underthrusts, bounding to the east with an area of gentle folds (Ramos, 1992; Manceda and Figueroa, 1995).

ANALYSED SAMPLES

The analysed samples belong to four outcrop and quarry sections located at arroyo Las Leñitas, Cañada Ancha and arroyo Blanco localities (Fig. 1). These sections were measured and surveyed at 1:100 and 1:200 scale, paying special attention to the lithologic composition, sedimentary structures, and bedding patterns.

The carbonate phase is mainly represented by calcite (LMC). Ca-sulphate phases are anhydrite and secondary
gypsum, the latter derived from the hydration of a precursor anhydrite phase as revealed by the petrographic study of the samples. Gypsum lithofacies include laminated, banded and micronodular secondary gypsum. Secondary gypsum crystalline fabrics are mostly represented by the alabastrine and megacrystalline varieties (Lo Forte, 2003). Although the original crystalline fabrics have been changed with the successive mineralogical transformations, the macroscopic structures (lithofacies) of the rocks remain little altered or unchanged because the anhydrite-to-secondary gypsum conversion is considered to be mainly an isovolumetric process.

The isotopic analyses were carried out in selected secondary gypsum samples; in all of them the mineralogical composition was controlled by conventional petrographic analysis and by X-ray diffraction (XRD).

**ANALYTICAL PROCEDURES**

Oxygen ($\delta^{18}O$) and sulphur ($\delta^{34}S$) isotopic compositions were analysed in ten samples of secondary gypsum following the procedures of Longinelli and Craig (1967) for oxygen and Robinson and Kusakabe (1975) for sulphur. In order to eliminate the CO$_2$ produced by the carbonate mineral matrix, samples were washed with 2N HCl. The CO$_2$ and SO$_2$ were analysed on a mass-spectrometer VG ISOGAS SIRA series 10 and VG ISOGAS SIRA series II respectively. Oxygen isotopic values are referred to the SMOW standard (Standard Mean Ocean Water; Craig, 1961) while sulphur isotopic values are referred to the CDT standard (Cañon Diablo Troilite; Jensen and Nakai, 1962). In all cases the analytical precision is ± 0.1‰. Isotopic measurements were carried out at the Servicio General de Análisis de Isótopos Estables of the Universidad de Salamanca (Spain).

The $\delta^{87}$Sr/$\delta^{86}$Sr ratios were determined in six gypsum samples at the Laboratorio de Geocronología y Geoquímica Isotópica of the Universidad Complutense de Madrid (Spain). Powdered samples were diluted and washed with 2.5 N HCl was separated and concentrated using a chromatographic column with DOWEX 50W*8 200/400 resin. Strontium isotopic analyses were performed on a TIMS VG SECTOR 54 mass-spectrometer. Values were corrected for the presence of $^{87}$Rb and normalized to $^{86}$Sr/$^{88}$Sr = 0.1194. The value of measured isotopic standard referred to NBS-987 was $^{87}$Sr/$^{86}$Sr = 0.71026 ± 0.00002 (2σ; n=7). The analytic error in the $^{86}$Sr/$^{88}$Sr ratio, referred to two standard deviations, is 0.01%.

**ISOTOPIC GEOCHEMISTRY**

The oxygen and the sulphur isotope compositions were analysed in three samples from the Tábanos Formation and seven samples from the Auquilco Formation; individual results and averages for each sample are summarised in Table 1. The oxygen and sulphur isotopic compositions are relatively uniform, averaging $+13.25\%$, with a $+11.55\%$ minimum value and a $+14.42\%$ maximum value for oxygen, and $+17.80\%$ in average, with a $+17.25\%$ minimum value and a $+18.48\%$ maximum value for sulphur. The comparison between the $\delta^{18}O$ and $\delta^{34}S$ values, shown in Figure 3, reflects this homogeneity without an evident data set clustering, even between both formations.

Six of these samples, one from the Tábanos Formation and five from the Auquilco Formation, were also analysed for strontium isotopes. The results gave an average of 0.706815 and minimum and maximum values ranging from 0.706793 to 0.706839; the detailed results for each sample are presented in Table 2. These isotopic values are also relatively uniform, as can be appreciated comparing the strontium isotopic ratios with the oxygen and sulphur isotopic compositions (Fig. 4).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fm.</th>
<th>$\delta^{34}S$ %e</th>
<th>$\delta^{18}O$ %e</th>
<th>Average $\delta^{34}S$ %e</th>
<th>Average $\delta^{18}O$ %e</th>
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<tr>
<td>A1</td>
<td>Tab.</td>
<td>+18.28</td>
<td>+13.27</td>
<td>+18.48</td>
<td>+13.83</td>
</tr>
<tr>
<td>A20</td>
<td>Auq.</td>
<td>+18.24</td>
<td>+14.27</td>
<td>+18.37</td>
<td>+14.70</td>
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<td>A*3</td>
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<td>+17.56</td>
<td>+13.13</td>
<td>+17.70</td>
<td>+13.11</td>
</tr>
<tr>
<td>C1</td>
<td>Auq.</td>
<td>+18.16</td>
<td>+13.08</td>
<td>+18.06</td>
<td>+13.15</td>
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<tr>
<td>C11</td>
<td>Auq.</td>
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<td>+13.14</td>
<td>+17.28</td>
<td>+13.12</td>
</tr>
<tr>
<td>C5</td>
<td>Auq.</td>
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<td>+13.12</td>
<td>+18.11</td>
<td>+13.49</td>
</tr>
<tr>
<td>C7</td>
<td>Auq.</td>
<td>+17.14</td>
<td>+14.16</td>
<td>+17.25</td>
<td>+14.14</td>
</tr>
<tr>
<td>D4</td>
<td>Auq.</td>
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<td>+14.14</td>
<td>+17.30</td>
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<tr>
<td>D6</td>
<td>Auq.</td>
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<td>+14.12</td>
<td>+17.43</td>
<td>+14.14</td>
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<tr>
<td>E7</td>
<td>Tab.</td>
<td>+18.00</td>
<td>+13.95</td>
<td>+18.00</td>
<td>+13.88</td>
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</table>

**TABLE 1** Isotopic composition ($\delta^{18}O$, $\delta^{34}S$) of secondary gypsum samples
DISCUSSION

Since the 1970’s considerable effort has been focused on the isotopic variation of marine sediments and seawater composition through time. Analyses of the $\delta^{18}O$, $\delta^{34}S$ and $^{87}Sr/^{86}Sr$ ratios in different marine carbonates and evaporites have shown a considerable variation for all three isotopes (Claypool et al., 1980; Burke et al., 1982).

Regarding the isotopic composition of the dissolved sulphate anion, sulphur values exhibit a greater variation than oxygen through geologic time due to its larger time-oscillation and to its low exchange ratio with seawater. Strontium isotope ratios are more sensitive than the sulphur isotopic composition to the incorporation of non-marine waters (hydrothermal or meteoric) to marine brines, since the strontium content is relatively low in marine brines but can be higher in non-marine waters. Thus, the contribution of small amounts of non-marine waters to restricted seawater bodies can alter the marine strontium isotopic signal and give higher values.

The relationships between the $\delta^{18}O$ and $\delta^{34}S$ values, shown in Figure 3 and Table 1, reflect homogeneity and clustering within the range of Jurassic evaporites. A number of Upper Jurassic formations analysed by Claypool et al. (1980; appendix) have $\delta^{34}S$ comprised between +15.4 and +17.5‰. Although the range of $\delta^{34}S$ values obtained in the present paper is slightly higher (between +17.25‰ and +18.48‰), it fits the Jurassic uncertainty area of the sulphur curve of Claypool et al. (1980) and the Jurassic values presented by Strauss (1997). Moreover, $\delta^{34}S$ values up to +19.2‰ have been reported in the literature (Utrilla et al., 1992) for marine anhydrites of Liassic age.

**TABLE 2** Strontium isotopic composition ($^{87}Sr/^{86}Sr$) of secondary gypsum samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Formation</th>
<th>$^{87}Sr/^{86}Sr$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Auq.</td>
<td>0.706825</td>
</tr>
<tr>
<td>C5</td>
<td>Auq.</td>
<td>0.706837</td>
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<tr>
<td>C7</td>
<td>Auq.</td>
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<td>C11</td>
<td>Auq.</td>
<td>0.706839</td>
</tr>
<tr>
<td>A*3</td>
<td>Tab.</td>
<td>0.706793</td>
</tr>
<tr>
<td>A20</td>
<td>Auq.</td>
<td>0.706794</td>
</tr>
</tbody>
</table>

**FIGURE 3** $\delta^{34}S$ versus $\delta^{18}O$ plot of analysed gypsum samples. Open circles: Tábanos Fm; filled circles: Auquilco Fm. Dashed area represents Jurassic values of marine evaporites (from Claypool et al., 1980).

**FIGURE 4** A) $^{87}Sr/^{86}Sr$ versus $\delta^{34}S$, and B) $^{87}Sr/^{86}Sr$ versus $\delta^{18}O$ plots of analysed gypsum samples. Open circles: Tábanos Fm; filled circles: Auquilco Fm. Dashed areas represent Jurassic values of marine evaporites (from Claypool et al., 1980, and Burke et al., 1982).
as also pointed out by Strauss (1997). Concerning the strontium isotope ratios, they also reflect certain homogeneity (Fig. 4 and Table 2) as well as a marine origin, as they are almost identical to the Upper Jurassic marine curve.

The comparison between the oxygen, sulphur, and strontium isotopic values obtained from our gypsum samples, and those values characteristic of Jurassic marine evaporites, is shown in Figure 5. The minimum and the maximum values of $^\delta^{18}O$, $^\delta^{34}S$ and $^{87}Sr/^{86}Sr$ have been plotted on the geohistoric curves of Claypool et al. (1980) for oxygen and sulphur, and of Burke et al. (1982) for strontium ratio. These results (Fig. 5) are also in agreement with biostratigraphic constraints (Riccardi, 1983; Riccardi et al., 2000).

We conclude that the analysed samples of secondary gypsum retained their original isotopic (marine) signal throughout the complete diagenetic cycle of calcium sulphate.

Our results are in agreement with the isotopic $^\delta^{34}S$ data and $^{87}Sr/^{86}Sr$ ratios reported by Brodtkorb et al. (1997) in the southern part of the basin (Neuquén province). Brodtkorb et al. (1997) analysed samples from secondary gypsum, anhydrite and celestite, and obtained values that were consistent with those of the Jurassic marine evaporites. Gypsum samples had $^{87}Sr/^{86}Sr$ values ranging from 0.70684 to 0.70728 and $^\delta^{34}S$ mean values of +16‰ (Tábanos Formation) and +16.8‰ (Auquilco Formation). Recently, Linares et al. (2003) have contributed new $^\delta^{34}S$ data for the Auquilco Formation, sampled at arroyo Negro near the Malargüe city, although in this case the $^\delta^{34}S$ values show a slightly lower mean (+15.3‰).

CONCLUDING REMARKS

The sulphur isotopic composition of the Ca-sulphate facies of the Jurassic Tábanos and Auquilco evaporitic sequences cropping-out in the Aconcagua-Neuquén Basin shows mean values of $+13.25\%e$ for $^\delta^{18}O$ and $+17.80\%e$ for $^\delta^{34}S$, all of them consistent with those of the Jurassic marine evaporites, according to published data (Claypool et al., 1980). Likewise, the $^{87}Sr/^{86}Sr$ ratios, ranging from 0.706793 to 0.706839, depict a good correspondence between our values and those corresponding to the Jurassic marine evaporites in the geohistoric curve of Burke et al. (1982). Despite their secondary character (i.e. the provenance from a precursor anhydritic phase), the analysed gypsum samples are valuable material for isotopic studies, because they have retained the original marine isotopic signal apparently unaffected by diagenesis. These results also suggest the absence of a significant contribution of continental waters or hydrothermal solutions, at least in an analytically detectable proportion, in the studied area of the basin.

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