Of Lower Cretaceous strata, 
Sierra San José section, Sonora (Mexico) 

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Abstract: We used petrofacies analysis, carbon, oxygen and strontium isotope data to interpret the isotopic variations in the carbonate rocks of the Mural Formation of Sonora (Sierra San José section), Mexico. The petrographic study reveals a range of lithofacies from wackestone to packstone. The analyzed limestones show significant negative $\delta^{18}O$ values (-18.6 to -10.9 VPDB) and $\delta^{13}C$ values ranging from negative to positive (-2.6 to +2.5‰ VPDB). The absence of correlation between $\delta^{13}C$ and $\delta^{18}O$ values suggests a primary marine origin for the $\delta^{13}C$ values of limestones from the Sierra San José section. The limestones have large variations in $^{87}Sr/^{86}Sr$ values (0.707479 to 0.708790). Higher $^{87}Sr/^{86}Sr$ ratios in various levels of the studied section suggest that most of the sediments were derived from the Proterozoic basement of the Caborca block during Early Cretaceous time. A decrease in $^{87}Sr/^{86}Sr$ ratios at certain levels indicates an influx of lesser amounts of radiogenic Sr that could have been caused by contribution of sediments from the Triassic and Jurassic volcanic rocks.

Key Words: Aptian-Albian stages; Mexico; Mural Formation biostratigraphy; stable isotopes; strontium isotopes.

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Résumé : Faciès, biostratigraphie, diagenèse et environnements de dépôt des couches du Crétacé inférieur d’une coupe de la Sierra San José, Sonora (Mexique).- Nous avons utilisé l’analyse pétrofaciologique et les données isotopiques du carbone, de l’oxygène et du strontium pour interpréter les variations isotopiques enregistrées par les roches carbonatées de la Formation Mural (coupe de la Sierra San José) de Sonora, Mexique. Il ressort de l’étude pétrographique que les lithofaciès ont des textures soit de type wackestone, soit de type packstone. Les calcaires analysés présentent des valeurs fortement négatives du $\delta^{18}O$ (comprises entre -18,6 et -10,9 VPDB) alors que celles du $\delta^{13}C$ varient de négatives à positives (de -2,6 à +2,5‰ VPDB). L’absence de corrélation entre les valeurs du $\delta^{13}C$ et celles du $\delta^{18}O$ suggère une origine marine primaire pour les valeurs du $\delta^{13}C$ des calcaires de cette coupe de la Sierra San José. Les calcaires analysés ont également enregistré de fortes variations des valeurs du rapport $^{87}Sr/^{86}Sr$ (de 0,707479 à 0,708790). Les rapports $^{87}Sr/^{86}Sr$ des plus forts rencontrés à différents niveaux de la coupe étudiée suggèrent qu’au Crétacé inférieur la plus grande partie des apports sédimentaires provienne du substratum protérozoïque du bloc Caborca. Une baisse dans les rapports $^{87}Sr/^{86}Sr$ de certains niveaux révèle des apports moindres en Sr radiogénique qui pourraient, cette fois-ci, être liés à une contribution de sédiments dérivés de roches volcaniques triasiques et jurassiques.

Mots-clés : Étages Aptien-Albien ; Mexique ; biostratigraphie de la Formation Mural ; isotopes stables ; isotopes du strontium.
1. Introduction

The stable isotopic compositions along with petrographic information of carbonate rocks may prove to be an important tool in tracing the fluid origin and in reconstructing large-scale movements and evolution of fluids (ALLAN and MATTHEWS, 1982). The carbon and oxygen isotopic composition of the carbonate sediments/rocks reflect the physicochemical properties of the waters, in which the sediment-contributing organisms grow (MORRISON and BRAND, 1986) and also provides information regarding the diagenetic processes and environments, which initiate the conversion of skeletal carbonates into limestones (JENKINS et al., 1994). The carbon and oxygen isotopic composition of carbonate rocks also provides valuable information regarding the temperature of deposition (ALI, 1995; CONIGLIO et al., 2000), source of carbonate (HUDSON, 1977; GAO et al., 1996; KUMAR et al., 2002; POULSON and JOHN, 2003), and/or palaeoclimate (QUADE and CERLING, 1995; SRIVASTAVA, 2001; SCOTT, 2002).

Carbonate rocks deposited in marine environments mainly record the carbon isotopic composition of the ocean water (SCHOLLE and ARTHUR, 1980). Similarly, oxygen isotope studies from foraminifers and the paleobotanical record provide strong evidence that the Cretaceous Period was substantially warmer than today (CROWLEY and NORTH, 1991; STEUBER et al., 2005). Paleoclimatic conditions for a given region can be determined by studying temporal changes of meteoric diagenesis within a single lithology, particularly limestone, and the geochemical signature of the associated diagenetic products (JAMES and CROQUETTE, 1984). Isotopic studies on shallow marine Lower Cretaceous carbonate rocks have shown evidence of paleoceanographic processes (KUMAR et al., 2002; MADHAVARAJU et al., 2004), climatic and biotic changes (DESHPANDE et al., 2003; MISHRA et al., 2010; PRÉAT et al., 2010; TEWARI et al., 2010) and global-scale tectonics (GRÖCKE et al., 2005; MAHESHWARI et al., 2005; AMODIO et al., 2008).

Figure 1: Location map of the Sierra San José section of the Mural Formation.
Lower Cretaceous Bisbee Group sedimentary rocks are well exposed in northern Sonora, Mexico. Extensive research activities have been undertaken on the Bisbee Group by various paleontologists and stratigraphers during the past decades, but detailed isotopic studies on the carbonate rocks are scanty and to date few studies have been undertaken on specific sections of the sedimentary rocks of the Mural Formation. Madhavaraju et al. (2013a, 2013b) carried out carbon, oxygen and strontium isotope studies on the limestones collected from the Cerro Pimas section (proximal part of the Bisbee basin) and Cerro El Caloso Pitayacachi section (distal part of the basin) to understand the paleoceanographic changes that occurred during the Early Cretaceous Epoch. Here we present carbon, oxygen and strontium isotope data from the northeastern part of the Bisbee basin exposed in the Sierra San José (Fig. 1). The objectives of the present study are: 1) To study the diagenetic changes in the carbon and oxygen isotopes; 2) to compare the carbon and oxygen isotopes of the section with that of the Mural Formation of Sonora (Madhavaraju et al., 2013a, 2013b); 3) to identify strontium isotopic variations in these carbonate rocks; and 4) to assess the probable reasons for the fluctuations in \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios.

2. Geology of the study area

The Lower Cretaceous Bisbee Group is well exposed in the north-central part of Sonora, Mexico, and has similar stratigraphic characteristics and is correlative with similar rocks exposed in southern Arizona and New Mexico in the United States of America (Ransome, 1904; Cantu-Chapa, 1976; Bilodeau and Lindberg, 1983; Mack et al., 1986; Dickinson et al., 1989; Jacques Ayala, 1995; Lawton et al., 2004). The sedimentary rocks of the Bisbee Group consist of four formations: Glance Conglomerate, Morita Formation, Mural Formation, and Cintura Formation. The Glance Conglomerate mainly consists of cobbles and boulders of metamorphic and granitic rocks locally interbedded with volcanic flows and tuffs that represent syntectonic rift deposits (Bilodeau et al., 1987). The Morita and Cintura formations include reddish brown siltstone and lenticular beds of arkose and feldspathic arenite (Klute, 1991) deposited in fluvial environments. Fossilliferous clastic and carbonate units of the Mural Formation overlie the Morita Formation and represent major Aptian-Albian marine transgression (Scott, 1987). Lawton et al. (2004) defined six members in the Mural Formation of Sonora (Fig. 2): Cerro La Ceja, Tuape Shale, Los Coyotes, Cerro La Puerta, Cerro La Espina, and Mesa Quemada members. These members are laterally persistent from northeastern to northwestern Sonora, in a 300 km-long transect showing only minor facies changes through several measured sections (González-León et al., 2008).

The Mural Formation exposed in the Sierra San José was deposited in the Bisbee Basin, which extended southeastward into the Chihuahua Trough (Fig. 1) (Lawton et al., 2004). The Sierra San José section spans from the basal Cerro La Ceja Member of the Mural Formation to the Mesa Quemada Member at the top (Fig. 2) (González-León et al., 2008; Madhavaraju et al., 2010). Previous studies demonstrated that the formation ranges from upper Aptian to lower Albian. Prominent age-diagnostic fossils present in thin sections of the Sierra San José outcrop are benthic foraminifera; calcareous algae are rarely present but invariably long ranging. This low-diversity biota is consistent with the published late Aptian to early Albian age of strata in this section (Lawton et al., 2004; González-León et al., 2008).

3. Methodology

Carbon and oxygen isotopic compositions were analyzed for eighteen samples using a Prism series II model mass spectrometer at Korea Basic Science Institute. The limestone samples were treated with H_3PO_4 in vacuum at 25°C and the resulted CO_2 gas analyzed following the standard method of McCrea (1950). Results are reported in the standard per mil (‰) δ-notations relative to the Pee Dee Formation Belemnite (PDB) marine carbonate standard. Sample reproducibility is better than ±0.05‰ for carbon and ±0.1‰ for oxygen.

Eighteen whole rock samples were analyzed for Sr isotope composition using a VG 54-30 thermal ionization mass spectrometer equipped with nine Faraday cups at Korea Basic Science Institute. Several 10 mg of whole-rock powders were mixed with highly enriched \(^{86}\text{Sr}\) and \(^{87}\text{Rb}\) spikes and then dissolved with a HF/HClO_4 acid (10:1) in Teflon vessels. Rb and Sr fractions were separated by conventional cation column chemistry (Dowex AG50W-X8, H+ form) in HCl medium. Instrumental fractionation was normalized to \(^{86}\text{Sr}/^{88}\text{Sr} = 0.1194\) and the measured \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios were further corrected for the contributions of the added spikes. Replicate analysis of NBS 987 gave a mean \(^{87}\text{Sr}/^{86}\text{Sr}\) of 0.7102450 ± 0.000003 (n = 30, 2σ SE). Total procedural blank levels were below 100 pg for Sr. The \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios are presented after adjusting them to NBS 987 \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio of 0.710230 (Verma, 1992; Verma and Hasenaka, 2004).
Figure 2: Lithostratigraphic section of the Mural Formation in Sierra San José area (modified after GONZÁLEZ-LEÓN et al., 2008). Member designations: CLC - Cerro La Ceja; TS - Tuape Shale; LC - Los Coyotes; CLP - Cerro La Puerta; CLE - Cerro La Espina; MQ - Mesa Quemada. San José outcrop sample numbers are Sj, which for thin sections and geochemical samples were changed to SSJ. Base of section at UTM 597021; 3455384; elevation 1761 m above SL.

4. Results

4.a. Biostratigraphy

Few short-ranging taxa are identifiable in the thin sections from our measured section at Sierra San José (Fig. 3). The new data do not alter previously published Aptian-lower Albian correlations of these formations. A benthic foraminifer in the Cerro La Espina Member of the Mural Formation, Paracoskinolina sunnilandensis (MAYNC) (Fig. 3.6-7), is a lower Albian species, reported elsewhere in the Bisbee Basin (LAWTON et al., 2004; GONZÁLEZ-LEÓN et al., 2008), which is common in the Trinity Group in Texas (SCOTT et al., 2003). Specimens of Mesorbitolina most likely are M. texana (ROEMER), which in the Trinity Group ranges in age from 113.70-108.19 Ma (SCOTT, 2014). However, the key protoconch and deuteroconch structures necessary to identify the species were not present in the available thin sections. The benthic foraminifer, Buccicrenata subgoodlandensis (VANDERPOOL), is rare in the Los Coyotes Member and is characteristic of the Trinity and Fredericksburg groups.

A small, conical benthic foraminifera in the Cerro La Puerta and Cerro La Espina members is Novalesia producta (MAGNIEZ) (Fig. 3.1-5), which ranges from late Aptian to early Albian (ARNAUD-VANNEAU and SLITER, 1995). The biserial genus Novalesia differs from the biserial cuneolinid genus Vercorsella by its conical test, by its thin radial septa that do not join the median septum, and by the slit-shaped aperture (LOEBLICH and TAPPAN, 1988). Novalesia was widespread in the Tethys from Spain, France and the Pacific seamounts (ARNAUD-VANNEAU and SLITER, 1995). Caprinid fragments of partial valve margins in the Los Coyotes Member have elongate oval pallial canals that diverge at the outer shell layer. The canals of these fragments are similar to those of Coalcomana, which is the distinctive and common genus in early Albian strata (SCOTT and FILKORN, 2007). However complete specimens are needed to verify the identification.

Table 1: Petrographic check-list of thin sections.
| Lithostratigraphy | Sample No. | Position in section from base | Micrites | Grain Types | Accessory Minerals | Indic. Bivalve | Ostracodes | Foraminifers | Micrites | Porousness | Pyritization | Lithology | Comments | Notes | Percent Quartz silt-sand | Opaque minerals | Mean BSE-874 |
|-------------------|------------|-------------------------------|----------|-------------|-------------------|--------------|-----------|-------------|----------|------------|-------------|-----------|-----------|-------|------------------------|---------------|------------|
| Cerro La Espina   | SSJ27      | 429                           | Lime mudstone | bioclasts | qtz silt          |              |           |             |          |            |             | MQM       |           |       | chert in shell          | <1            | T - organics? 0.708 |
|                   | SSJ25      | 373                           | Mollusk wackestone | bioclasts, peloids | F C R           |              |           |             |          |            |             | MQM       |           |       | fat orbits, nannoliths   | 0             | T - hematite & organics? 0.708 |
|                   | SSJ23      | 329                           | Sandy Coral- Caprinid packstone | bioclasts, peloids | F C R T |              |           |             |          |            |             | MQM       |           |       | chert fracture; stylolite | 3             | T - hematite & organics? |
| Cerro La Puerta   | SSJ20      | 274                           | Caprinid- algal boundstone | bioclasts, peloids | A T R R R R R |              |           |             |          |            |             | MQM       |           |       |                        |               | 0.708       |
|                   | SSJ19      | 244                           | Caprinid packstone | bioclasts, peloids | A A F R R ? F T T |              |           |          |          |            |             | MQM       |           |       |                        |               | 0.708       |
|                   | SSJ18      | 242                           | Caprinid wackestone | bioclasts | hematite          |              |           |             |          |            |             | MQM       |           |       |                        |               | 0.708       |
|                   | SSJ16      | 240                           | Caprinid wackestone | bioclasts | chert |              |           |             |          |            |             | MQM       |           |       |                        |               | 0.708       |
|                   | SSJ13      | 239                           | Orbitolinid wackestone | bioclasts, peloids | R R T T T R R |              |           |             |          |            |             | MQM       |           |       |                        |               | 0.708       |
| Los Coyotes       | SSJ11      | 237                           | Orbitolinid wackestone | bioclasts, peloids | R R A A T T R F |              |           |             |          |            |             | MQM       |           |       |                        |               | 0.708       |
|                   | SSJ10      | 227                           | Orbitolinid wackestone | bioclasts | R F F T T T F R |              |           |             |          |            |             | MQM       |           |       |                        |               | 0.708       |
| Tuape Shale       | SSJ7       | 192                           | Silty Bioclastic packstone | bioclasts, im midt intraclasts | A R   |              |           |             |          |            |             | MQM       |           |       |                        |               | 0.708       |
|                   | SSJ6       | 146.5                         | Bioclastic calc sandstone | bioclasts | ang-subrd qtz silt |              |           |             |          |            |             | MQM       |           |       |                        |               | 0.708       |
|                   | SSJ5       | 85                            | Silty lime wackestone | bioclasts | qtz, chert nodules |              |           |             |          |            |             | MQM       |           |       |                        |               | 0.708       |
|                   | SSJ4       | 73                             | Silty lime mudstone | bioclasts | ang silt qtz, chert nodules |              |           |             |          |            |             | MQM       |           |       |                        |               | 0.708       |
|                   | SSJ3       | 23                             | Sandy bioclastic wackestone | bioclasts | subang-subrd fr gr qtz, chert nodules |              |           |             |          |            |             | MQM       |           |       |                        |               | 0.708       |
|                   | SSJ2       | 10                             | sandy bioclastic mudstone | bioclasts | qtz, phosphate, chert |              |           |             |          |            |             | MQM       |           |       |                        |               | 0.708       |
A single planktic foraminifer specimen in the Cerro La Puerta Member is tentatively identified as *Clavihedbergella* sp., because of its axial profile (Fig. 3.8). This genus ranges from Barremian-Aptian to Coniacian (LOEBLICH and TAPPAN, 1988; SCOTT, 2014). To confirm the identification of the genus and species a transverse view showing the whorl expansion is needed. *Clavihedbergella simplex* (MORROW) is present in the upper Aptian-lower Albian interval (113.43-86.83 Ma; SCOTT, 2014).

4.b. Lithofacies and depositional environments

Petrographic data are from eighteen thin section samples of members of the Mural Formation (Table 1). The members of the Mural represent two longer-term depositional cycles: 1) the Cerro La Ceja, Tuape Shale and Los Coyotes cycle and 2) the Cerro La Puerta, Cerro La Espina and the Mesa Quemada cycle (Fig. 2) (LAWTON et al., 2004; GONZÁLEZ-LEÓN et al., 2008). The overlying Cintura Formation represents a major shift in basin deposition from mixed carbonate and siliciclastic sediment to dominantly siliciclastic sediment.

The *Cerro La Ceja Member* at the base of the section is composed of shale and thin-bedded sandstone and limestone (Table 1; Fig. 4.1). The samples are sandy bioclastic mudstone and wackestone with phosphate nodules and chert grains. Fine-grained quartz grains are subangular to subrounded. The biota consists of indeterminate bivalves, foraminifers, echinoderms, and ostracodes. Wavy stylolites suggest burial to moderate depths. These strata were deposited on a nearshore shallow shelf during transgression (LAWTON et al., 2004). The *Tuape Shale* is dominantly shale with thin beds of limestone (Table 1; Fig. 4.2). The main limestone facies are silty lime wackestone and mudstone with chert nodules. Quartz grains are angular silt to fine sand. The biota consists of indeterminate bivalves, oyster, ostracodes, and foraminifera. Wavy stylolites are crossect by fractures. This unit was deposited on a deep offshore shelf near local biotic buildups during maximum flooding. Farther southeast in the basin euxinic conditions prevailed (LAWTON et al., 2004). Two samples of the *Los Coyotes Member* are composed of bioclastic calcareous sandstone and bioclastic packstone microfacies (Table 1; Fig. 4.3). The sparse biota is composed of indeterminate bivalves, foraminifera and echinoids. Wavy stylolites are cut by fractures. The depositional environment of the *Cerro Los Coyotes Member* was a shallow shelf complex with buildups and shoaling-up small-scale bed cycles during highstand conditions. Paleobathymetry was mainly within the local photic zone. This member records progradation and shoaling (LAWTON et al., 2004).
Figure 4: Mural Formation lithofacies and diagenetic features. Scale bar = 1 mm.
1. Cerro La Ceja Member, sandy bioclastic wackestone, SS13 (9-14-3);
2. Tuape Shale, silty wackestone, note recrystallized bivalve bioclasts, SS15 (9-14-5);
3. Los coyotes Member, silty bioclastic packstone, note calcite-filled fracture and recrystallized bivalve bioclasts, SSJ7 (9-14-7);
4. Cerro La Puerta Member, orbitolinid packstone, note calcite-filled fracture, SSJ11 (9-15-2);
5-10. Cerro La Espina Member, SSJ13-16, 19-20, 23-25 (9-15-4, -7, -10, -11, -14, -16);
5. Orbitolinid wackestone, note fracture set filled with secondary calcite, SSJ13 (9-15-4);
6. Caprinid packstone, oblique cross section of caprinid pallial canals, SSJ16 (9-15-7);
7. Caprinid packstone, *Paracoskinolina sunnilandensis* (Maync) among bioclasts, SSJ19 (9-15-10);
8. Caprinid-algal boundstone, colonial coral encrusted by multiple algal laminae, SSJ20 (9-15-11);
9. Sandy coral-caprinid packstone; note encrusted colonial coral, SSJ23 (9-15-14);
10. Mollusk wackestone, note gastropod, SSJ25 (9-15-16).
The Cerro La Puerta Member is represented by orbitolinid wackestone-packstone (Table 1; Fig. 4.4). Biota is composed of indeterminate bivalves, gastropods, foraminifers including Mesorbitolina, Novalesia, Lenticulina, the planktic foraminifera Clavihebedbergella, and encrusting foraminifera, and ostracodes. Sub-parallel fracture sets are filled with calcite. Deposition was on offshore shallow shelf and represents flooding during a second depositional cycle (Lawton et al., 2004). The Cerro La Espina Member is composed of multiple facies in vertical succession from base to top: orbitolinid wackestone, caprinid wackestone-packstone, caprinid-algal boundstone, sandy coral-caprinid packstone, and capped by mollusk wackestone (Table 1; Fig. 4.5-10). Caprinids are common to abundant; colonial corals are common in one sample; calcareous algae and stromatoporoids are rare; associated biota consists of echinoderms, benthic foraminifera, and ostracodes. Peloids are common in the Cerro La Espina Member; quartz sand is fine to medium, subangular to subrounded. Locally poikilotopic calcite surrounds echinoderm parts. Chert nodules and quartz overgrowths in optical continuity with secondary chert partly replaces some bioclasts. Deposition was on shallow nearshore shelf; in other parts of the basin this member represents complex environments (Lawton et al., 2004).

4.c. Carbon and oxygen isotopic variations

The analyzed samples show large variations in carbon and oxygen isotope values (Table 2). The δ18O values range from -17.9 to -16.29‰ for the Cerro La Ceja member (CLC) (Table 2). The δ18O values of limestone in the Tuape Shale (TS) and Los Coyotes (LC) members vary little (-15.5 to -15.0‰; -14.7 to -13.8‰; respectively). The Cerro La Puerta (CLP) member has negative δ18O values from -15.5 to -13.8‰. The Cerro La Espina (CLE) member shows large variations in δ18O values (-18.6 to -10.9‰; Fig. 5). The Mesa Quemada (MQ) member also shows significant negative oxygen isotope values (-13.6‰).

Table 2: CaCO3, trace elements (Sr, Mn) and carbon and oxygen isotope values for limestones of the Mural Formation.

| Member/Sample No | CaCO3 | Mn | Sr | Mn/Sr | δ13C | δ18O | Z value* |
|------------------|-------|----|----|-------|------|------|---------|
| **Sierra San Jose Section** |       |    |    |       |      |      |         |
| Mesa Quemada SSJ27 | 87.61 | 3407 | 983 | 3.47 | -1.3 | -13.6 | 117.87  |
| **Cerro La Espina** |       |    |    |       |      |      |         |
| SSJ25            | 92.36 | 541 | 313 | 1.73 | 2.5  | -18.3 | 123.31  |
| SSJ23            | 90.41 | 150 | 390 | 0.38 | 1.2  | -10.9 | 124.33  |
| SSJ21            | 93.80 | 74  | 439 | 0.17 | 1.3  | -12.7 | 123.64  |
| SSJ20            | 94.15 | 80  | 410 | 0.20 | 1.5  | -14.8 | 123.00  |
| SSJ19            | 95.80 | 86  | 425 | 0.25 | 2.2  | -14.8 | 124.44  |
| SSJ18            | 97.46 | 77  | 407 | 0.19 | 2.3  | -15.4 | 124.34  |
| SSJ16            | 93.71 | 77  | 434 | 0.18 | 2.0  | -15.6 | 123.63  |
| SSJ13            | 95.20 | 94  | 395 | 0.24 | 1.7  | -18.6 | 121.52  |
| **Cerro La Puerta** |       |    |    |       |      |      |         |
| SSJ11            | 92.28 | 542 | 827 | 0.66 | 2.4  | -15.5 | 124.40  |
| SSJ10            | 93.82 | 154 | 849 | 0.18 | 3.2  | -15.4 | 126.18  |
| SSJ9             | 93.28 | 155 | 673 | 0.23 | 2.9  | -13.8 | 126.37  |
| **Los Coyotes** |       |    |    |       |      |      |         |
| SSJ7             | 91.41 | 618 | 1183| 0.52 | 1.1  | -13.8 | 122.68  |
| SSJ6             | 64.67 | 690 | 753 | 0.92 | -1.5 | -14.7 | 116.91  |
| **Tuape Shale** |       |    |    |       |      |      |         |
| SSJ5             | 82.32 | 620 | 699 | 0.89 | -2.5 | -15.5 | 114.46  |
| SSJ4             | 88.77 | 697 | 520 | 1.34 | 0.4  | -15.0 | 120.65  |
| **Cerro La Ceja** |       |    |    |       |      |      |         |
| SSJ3             | 66.53 | 2246| 528 | 4.25 | -2.6 | -16.2 | 113.91  |
| SSJ2             | 58.51 | 542 | 481 | 1.13 | -0.5 | -17.9 | 116.97  |
The $\delta^{13}C$ values in the CLC member are significantly negative to slightly positive (-2.6 to +0.5‰; Table 2). The TS and LC members exhibit both negative and positive carbon isotope values (-2.5 to +0.4‰; -1.5 to +1.1‰; respectively). The CLP member shows positive carbon isotope values (+2.4 to +3.2‰; Figs. 5-6). Likewise, limestone in the CLE member also has positive carbon isotope values (+1.2 to +2.5‰). The lone sample from the MQ member has a negative carbon isotope value (-1.3‰).

The strontium isotope composition of limestone of the Mural Formation is given in Table 3. The $^{87}\text{Sr}/^{86}\text{Sr}$ values of CLC Member vary from 0.708240 to 0.708320. The TS Member shows large variations in $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.708196 to 0.708790; Table 3). The $^{87}\text{Sr}/^{86}\text{Sr}$ values of LC Member vary between 0.707853 and 0.708078. The $^{87}\text{Sr}/^{86}\text{Sr}$ values of CLP Member vary from 0.707634 to 0.707880. Limestone in the CLE Member has large variations in $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.707479 to 0.708432). The MQ Member also has a higher $^{87}\text{Sr}/^{86}\text{Sr}$ value (0.707479) than the contemporary early Albian seawater values.
5. Discussion

5.a. Carbon and oxygen isotope composition

The limestones from the Sierra San José section show negative oxygen isotopic values (-18.6‰ to -10.9‰ VPDB) (Fig. 6). The lower part of the section shows slight variations in isotopic values whereas the middle part of the section shows large fluctuations. Likewise, the upper part of the section also exhibits more variations in the oxygen isotope values. The most negative values are observed in the lower part of the Cerro La Ceja and Cerro La Espina members and middle part of the Mesa Quemada Member. The lowest δ¹⁸O value (-18.6‰) occurs in the lower part of the CLE Member probably related to a sudden change in the sedimentation conditions and also due to the effects of early meteoric diagenesis (e.g., -2‰ to -15‰, Dickson, 1992). Marine limestones affected by diagenesis in general possess more negative δ¹⁸O values (Morse & Mackenzie, 1990; Land, 1970) because cementation and/or recrystallization commonly takes place in fluids depleted in δ¹⁸O with respect to sea water (e.g., meteoric water) or at elevated temperatures (burial conditions).
Figure 7: Chronostratigraphic interpretation of the Sierra San José section. Biostratigraphic data are from thin sections SSJ2 to SSJ27. The fossil ranges in the section are compared to their ages in the database CRETCSDB2, which is an earlier version of CRETCSDB4 (SCOTT, 2014). The FO and LO of *Novalesia producta* is projected into the LOC (dotted lines). The position of the Aptian/Albian boundary is uncertain but falls within the stratigraphic interval of the gray box.

Carbon isotopes are less affected by diagenetic alteration than oxygen isotopes (HUDSON, 1977; BANNER and HANSON, 1990; MARSHALL, 1992; FRANK et al., 1999), because of the buffering effect of carbonate carbon in the diagenetic system (PRICE et al., 2008). The correlation of $\delta^{13}C$ and $\delta^{18}O$ values of Mural Limestone in the Sierra San José section is not statistically significant ($r = 0.01, n = 18$; lack of statistically significant correlation (VERMA, 2005) (Fig. 5) indicates a lack of diagenetic influence on the carbon isotopic signatures (e.g.,
Another test of the diagenetic alteration of limestone is by the following equation: where \( Z = a (\delta^{13}C + 50) + b (\delta^{18}O + 50) \), in which \( a \) and \( b \) are 2.048 and 0.498 respectively (KEITH and WEBER, 1964). In this study of Mural Limestone the Z value discriminates between marine and freshwater limestone. Limestones with Z values above 120 are considered marine, whereas those with Z values below 120 would be classified as freshwater type. In the present study, the majority of limestones have Z values above 120, whereas few exhibit Z values below 120. This measure further supports that these limestones were least altered during diagenesis.

The carbon isotope curve shows two negative excursions in the lower part and one negative isotopic excursion in the upper part of the Sierra San José section. Most of the samples from the middle and upper part of the section show positive carbon isotope values (Fig. 6). An abrupt decrease in \( \delta^{13}C \) value is observed in the uppermost part of the section (SSI27: -1.3% VPDB). Sample SSI27 has a more negative value than limestone collected several meters below this sample (Fig. 6). Negative values of \( \delta^{13}C \) are mainly due to biogenic production of CO\(_2\) in the soil (CÉRLING and HAY, 1986) and indicate subaerial exposure, because of incorporation of lighter carbon isotope from soil-borne carbon dioxide and decay of terrestrial matter (HUDSON, 1977).

The positive isotopic excursion observed in the middle and upper parts of the Sierra San José section indicates the increasing impact of primary production in the photic zone, with associated organic burial rates exceeding those of its oxidative mineralization of organic matter (KUMP and ARTHUR, 1999). Variations in the \( \delta^{13}C \) signatures of shallow marine carbonates are widely used to interpret the primary variations in seawater \( \delta^{13}C \) during the Early Cretaceous (JENKYNs, 1995; VAHRKENAMP, 1996; GRÖTSCH et al., 1998; GRANIER, 2012, 2014). The \( \delta^{13}C \) values, of the present study suggests that the \( \delta^{13}C \) values measured from the Sierra San José section correspond to original seawater composition (mainly above 0 and below +3‰; FÖLLMI et al., 1994, 2006; MENEGATTI et al., 1998; BRALOWER et al., 1999; HERRLE et al., 2004; WISSLER et al., 2004). In addition, lack of correlation between \( \delta^{13}C \) and \( \delta^{18}O \) and the environmental significance of Z values also suggest that Mural limestones from the Sierra San José section exhibit primary carbon isotope signatures. Hence, most carbon isotope data of bulk rocks from the Sierra San José section of the Mural Formation are comparable with the published values of late Aptian - early Albian age.

5.b. Strontium Isotopes

The strontium isotopic record provides possible constraints on the importance of various factors that affect global weathering, rates and rock types being weathered, such as orogenic events (EDMOND, 1992) and glacial activity (HODELL et al., 1989), and the relative significance of postulated changes in mid-ocean ridge hydrothermal output (REA, 1992). The \( ^{87}Sr/^{86}Sr \) composition of seawater served as an important tool for stratigraphic correlations and indirect age assignment, reconstruction of global tectonics, and understanding of the diagenetic processes (BURKE et al., 1982; VEIZER, 1989; VEIZER et al., 1997, 1999; MCArTHUR et al., 1990; 1992a, 1992b, 1994, 2000; HOWARTH & MCArTHUR 1997; HALVERSON et al., 2007). The \( ^{87}Sr/^{86}Sr \) ratio of modern oceans (0.7092) is mainly a combination of detrital input from continental weathering (0.7120) and hydrothermal alteration of the oceanic crust (0.7035; EDMOND, 1992).

Overall, \( ^{87}Sr/^{86}Sr \) values of limestone in the Mural Formation at the Sierra San José section vary greatly from 0.707479 to 0.708790 (Table 3). Such large variations in \( ^{87}Sr/^{86}Sr \) values in limestone are largely controlled by diagenesis, hydrothermal input and riverine sources (relative proportion of young vs old silicate rocks undergoing weathering, TAYLOR and LASAGA, 1999).

5.c. Implication for Diagenesis

The trace elements variations have been considered to be an important tool to identify diagenetic alteration of ancient carbonate rocks (e.g., BRAND and VEIZER, 1980; JONES et al., 1994a, 1994b; PRICE and SELLWOOD, 1997; PODLAVA et al., 1998; HESSELBO et al., 2000; PRICE et al., 2000; JENKYNs et al., 2002; GROCKE et al., 2003; MADHAVARAJU et al., 2013a, 2013b). Mn may be incorporated and Sr may be expelled from the carbonate system during diagenesis (BRAND and VEIZER, 1980; VEIZER, 1983). The Mn/Sr ratio is useful to understand the diagenetic changes in the carbonate rocks (KAUFMAN et al., 1993; KAUFMAN and KNOLL, 1995; JACOBSEN and KAUFMAN, 1999). Marine limestones with Mn/Sr ratios less than 2 indicate that those limestones were least altered by diagenesis (JACOBSEN and KAUFMAN, 1999; SIAl et al., 2001; MARQUILLAS et al., 2007; NAGARAJAN et al., 2008; KAKIZAKI and KANO, 2009).

In the present study, the limestones of the Mural Formation have higher \( ^{87}Sr/^{86}Sr \) ratios than the contemporary Aptian-Albian seawater. Such elevated ratios in carbonate rocks may be influenced by diagenetic modifications. However, most of the studied samples have low Mn/Sr ratios less than 2 (Table 2) suggesting that the higher isotopic ratios have not been diagenetically altered.

5.d. Implications for Hydrothermal Input

The \( ^{87}Sr/^{86}Sr \) composition of seawater serves as an important tool for stratigraphic correlations and indirect numerical age assignments, reconstruction of global tectonics, and under-
standing diagenetic processes (Burke et al., 1982; Veizer, 1989; McArthur et al., 1990, 1992a, 1992b, 1994; Halverson et al., 2007). In addition, a significant amount of seawater-oceanic crust interaction takes place at low temperatures that contribute third components such as palagonite, smectite and/or carbonates (Jochum and Verma, 1996). Detailed studies of hydrothermal fluids provide important information regarding the seawater-oceanic crust interaction (Michard and Albarede, 1986; Piepgras and Wasserburg, 1986; Hinkley and Tatsumoto, 1987; Klinkhammer et al., 1994).

Sr that enters the ocean from hydrothermal systems along mid-ocean ridges has an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7027 (e.g., Allegre et al., 1983). The exact Sr-isotope evolution of MORB-source mantle is unknown, but hydrothermal alteration of oceanic crust results in a ratio of 0.7035 (Davis et al., 2003). The average composition of continental crust has not changed greatly since 3.7 Ga (e.g., Condie, 1993). The phenomenon is better interpreted to reflect a change in the ratio between hydrothermal and continental flux to the oceans, that is, the flux ratio (Derry and Jacobsen, 1988).

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of modern oceans (0.7092) is mainly a mixture of detrital input from continental weathering (0.7120) and hydrothermal alteration of the oceanic crust (0.7035; Davis et al., 2003). The lower limit of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is higher than the contemporary Early Albian (0.7073) seawater as well hydrothermal flux. Hydrothermal solutions mainly originate in the deep marine environments; however, such source is doubtful for the limestones of the Formation which were depo-

5.e. Implications for continental weathering

Sedimentologic observations suggest that the Mural Formation formed on a large, shallow marine shelf covering southern Arizona and northern Sonora. Our samples represent shallow marine depositional environments, including open marine settings. Hence, it is not surprising that the trace element and isotopic signatures of the samples reflect an environment where open marine waters (those with the most juvenile isotope signatures) mixed with estuarine waters that were more influenced by relatively local continental hinterland. However, the present study found a stronger distinction between open marine and continent-dominated water chemistries, which clearly requires that relatively local sources of terrestrial input from the hinterland. Mural Formation limestones show remarkable variations in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios among various members. Higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are observed in the CLC, TS and CLE members than in other members, a pattern which suggests that $^{87}\text{Sr}/^{86}\text{Sr}$ ratio fluctuations are related to the decrease in the riverine inputs. Units at the base of the section (CLC and TS members) have high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios followed by a gradual decrease in the Sr isotopic values in the LC and CLP members. Above in lower and middle parts of the CLE member the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio gradually increases, and in upper part of the CLE member the ratio abruptly falls, followed by an abrupt increase in $^{87}\text{Sr}/^{86}\text{Sr}$ values in the MQ member. Such short term reduction could have been caused by weathering rates of older crystalline rocks vs. younger volcanics and/or rising sea levels that reduced the area of continents exposed to weathering.

Probst et al. (2000) noted that during the weathering process Sr composition initially spikes and that $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range up to 0.7420. The relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the Sierra San José section of the Mural Formation suggests significant weathering of a granitic provenance. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of granites from Caborca block of Sonora is up to 0.7090 (Valencia-Moreno et al., 2001, 2003). The significant fluctuations in the $^{87}\text{Sr}/^{86}\text{Sr}$ values in the studied section may be related to variations in the episodic/periodic influx of siliciclastics from the provenance area.

According to Bullen et al. (1997), significant quantities of radiogenic Sr may be leached from K-feldspar during weathering of granitoid provenances. The source area of the Bisbee Basin in Sonora was mainly composed of granitic rocks that released significant amount of radiogenic Sr to these limestones through riverine Sr flux. So, high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at various levels in the Sierra San José section of the Mural Formation suggest that a considerable amount of sediments was contributed by Proterozoic basement of the Caborca block during Aptian-Albian age. The decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at certain levels of the studied section indicates a decreased influx of radiogenic Sr to the Mural Formation.

6. Chronostratigraphy and isotopic evolution

The Mural Formation members were correlated with the upper Aptian and lower Albian substages by ammonites, bivalves, and foraminifera (González-León et al., 2008). The stage boundary was correlated approximately with the Tuape Shale/Los Coyotes Member contact. In the Sierra San José section the Cerro La Espina and uppermost Cerro La Puerta members yield age-diagnostic fossils, but other members in the Sierra San José section have no diagnostic fossils as yet. A graphic plot of the Sierra San José section projects the Aptian/Albian boundary at approximately 200 m in the lower part of the Cerro La Puerta (Fig. 7). The age model (CRETCSDB) is defined by ranges of more than 3500 events in more than 200
sections (Scott, 2014). The line of correlation (LOC) is constrained by the first occurrence (FO) of Buccirecuta subgoodlandensis and the last occurrence (LO) of Mesorbitolina texana. In other sections in the region the lower Albian rudist, Coaacomana ramosa (Boehm), is reported in the Los Coyotes (González-León et al., 2008). Therefore the stage boundary is close to the base of the Los Coyotes and the LOC would be steeper than in Fig. 7, which would project events below 240 m slightly older than shown in Fig. 7.

Based on the graphic plot (Fig. 7) the bases of carbon isotope events 11, 12 and 13 are projected into the upper part of the Cerro La Puerta and the lower part of the Cerro La Espina members. The ages of carbon isotope events are projected from the Santa Rosa Canyon section (Bralower et al., 1999), where the base of C11 is a steep negative shift similar to the data at Sierra San José. The base of C12, which is a steep positive shift at Santa Rosa, is projected high in the Sierra San José section in a relatively flat interval (Fig. 7) above a distinct positive shift at 240 m. The position of Oceanic Anoxic Event 1b is projected from a number of deep oceanic sections and here spans from upper Cerro La Puerta to lower Cerro La Espina (Fig. 7). The range of carbon isotope data in the Sierra San José section is from -2.6 to 3.2 ppm, (Fig. 7). Therefore the stage boundary is close to the base of the Los Coyotes and the LOC would be steeper than in Fig. 7, which would project events below 240 m slightly older than shown in Fig. 7.

Conclusions

Limestones collected from the Sierra San José section of the Mural Formation are wackestone and packstone lithofacies. Mural Formation limestones consist mainly of both micrite and coarse grained carbonate. The negative δ18O isotope values and common rapid fluctuation in the δ18O profile the Mural Formation suggest diagenetic changes affected oxygen isotope values. The lack of correlation between δ13C and δ18O suggests that limestones exhibit primary carbon isotope signatures. The carbon isotope curve shows two negative excursions in the lower part and one negative isotopic excursion in the upper part of the Sierra San José section. Most of the samples from the middle and upper parts of the section have positive carbon isotope values. The δ13C values of limestone in the Sierra San José section suggest that the δ13C values represent original Albian seawater composition and in combination with chronostratigraphic data, that OAE 1b extended into the Bisbee Basin and infringed onto the carbonate shelf.

The 87Sr/86Sr ratio of Mural Formation limestones varies widely from 0.707497 to 0.708790. Higher 87Sr/86Sr ratios at various levels in the Sierra San José section suggest that a considerable amount of sediment was derived from the Proterozoic basement of the Caborca block during Early Cretaceous. The decrease in 87Sr/86Sr ratios recorded at certain levels of the studied section indicates a decrease in influx of radiogenic Sr to the Mural Formation.

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