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Neoproterozoic diamictite-cap carbonate succession and $\delta^{13}C$ chemostratigraphy from eastern Sonora, Mexico

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Abstract

Despite the occurrence of Neoproterozoic strata throughout the southwestern U.S. and Sonora, Mexico, glacial units overlain by enigmatic cap carbonates have not been well-documented south of Death Valley, California. Here, we describe in detail the first glaciogenic diamictite and cap carbonate succession from Mexico, found in the Cerro Las Bolas Group. The diamictite is exposed near Sahuaripa, Sonora, and is overlain by a 5 m thick very finely-laminated dolostone with soft sediment folds. Carbon isotopic chemostratigraphy of the finely-laminated dolostone reveals a negative $\delta^{13}C$ anomaly (down to −3.2‰ PDB) characteristic of cap carbonates worldwide. Carbon isotopic values rise to +10‰ across ~400 m of section in overlying carbonates of the Mina el Mezquite and Monteso Formations. The pattern recorded here is mostly characteristic of post-Sturtian (ca. ≤700 Ma), but pre-Marinoan (ca. ≥635 Ma) time. However, the Cerro Las Bolas Group shares ambiguity common to most Neoproterozoic successions: it lacks useful radiometric age constraints and biostratigraphically useful fossils, and its $\delta^{13}C$ signature is oscillatory and therefore somewhat equivocal.

Keywords: Neoproterozoic; Chemostratigraphy; Mexico; Sonora; Cap carbonate

1. Introduction

Many Neoproterozoic stratigraphic successions contain glacial deposits capped by enigmatic carbonate strata termed ‘cap carbonates’ (e.g., Kennedy, 1996; Kaufman et al., 1997; Hoffman et al., 1998a,b; Kennedy et al., 1998; Prave, 1999; James et al., 2001; Kennedy et al., 2001; Hoffman and Schrag, 2002; Corsetti and Kaufman, 2003; Rodrigues-Nogueira et al., 2003; Halverson et al., 2004; Lorentz et al., 2004; Porter et al., 2004; Xiao et al., 2004). Cap carbonates record negative $\delta^{13}C$ anomalies and many contain unusual carbonate fabrics such as seafloor-precipitated crystal fans and tubestones. This glacial-cap carbonate pattern and concomitant $\delta^{13}C$ anomaly is noted in almost every Neoproterozoic basin around the world and is thought by many to result from low-latitude glaciation and its aftermath. The fact that cap carbonates are also found in siliciclastic-dominated successions suggests that a global marine increase in the saturation state of calcium carbonate occurred and was associated with major perturbations in the carbon cycle. Although the source of the alkalinity, the causation of the negative $\delta^{13}C$

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anomalies, and the origin of the uncommon carbonate fabrics is the source of much debate, chemostratigraphic studies have used this repetitive lithostratigraphic and chemostratigraphic pattern to attempt regional and global correlations between poorly fossiliferous or radiometrically unconstrained Neoproterozoic successions (cf. Kennedy et al., 1998).

In western North America, the glacial-cap carbonate archetype is discontinuously exposed from the Death Valley region northward to the Mackenzie Mountains in northwestern Canada (Stewart and Suczek, 1977; Link et al., 1993; James et al., 2001; Lorentz et al., 2002; Corsetti and Kaufman, 2003; Lorentz et al., 2004). Despite widespread occurrence of Neoproterozoic strata south and east of Death Valley (Stewart et al., 1984, 2002; Stewart and Poole, 2002), glacial deposits and associated cap carbonates have not been recognized. Here, we describe in thin diamictite-carbonate couplet in the Sahuaripa area of southeastern Sonora (Fig. 1), examine its δ^{13}C profile, and discuss its significance with respect to the Neoproterozoic history of North America and elsewhere (see also Corsetti et al., 2001; Stewart et al., 2002). Southeastern Sonora resides at a critical crossroads with respect to Neoproterozoic plate reconstructions (Stewart et al., 2002) and thus the documentation of glacial-cap carbonate and concomitant chemostratigraphic profiles may provide additional paleogeographic and chronostratigraphic constraints for this region.

2. Geologic setting

Neoproterozoic strata in Sonora, Mexico can be subdivided into the 1) Caborca succession and equivalents to the northwest, 2) the El Aguila and Las Viboras Groups to the southeast, and 3) the Cerro Las Bolas Group to the far southeast (Stewart et al., 2002; Sour-Tovar et al., 2007). The Caborca succession and equivalents display clear lithostratigraphic similarity to Neoproterozoic–Cambrian Cordilleran miogeoclinal strata of Death Valley, California, and are commonly considered lateral equivalents to the Death Valley/White Inyo successions to the north that formed in response to late Neoproterozoic rifting of North America (Stewart

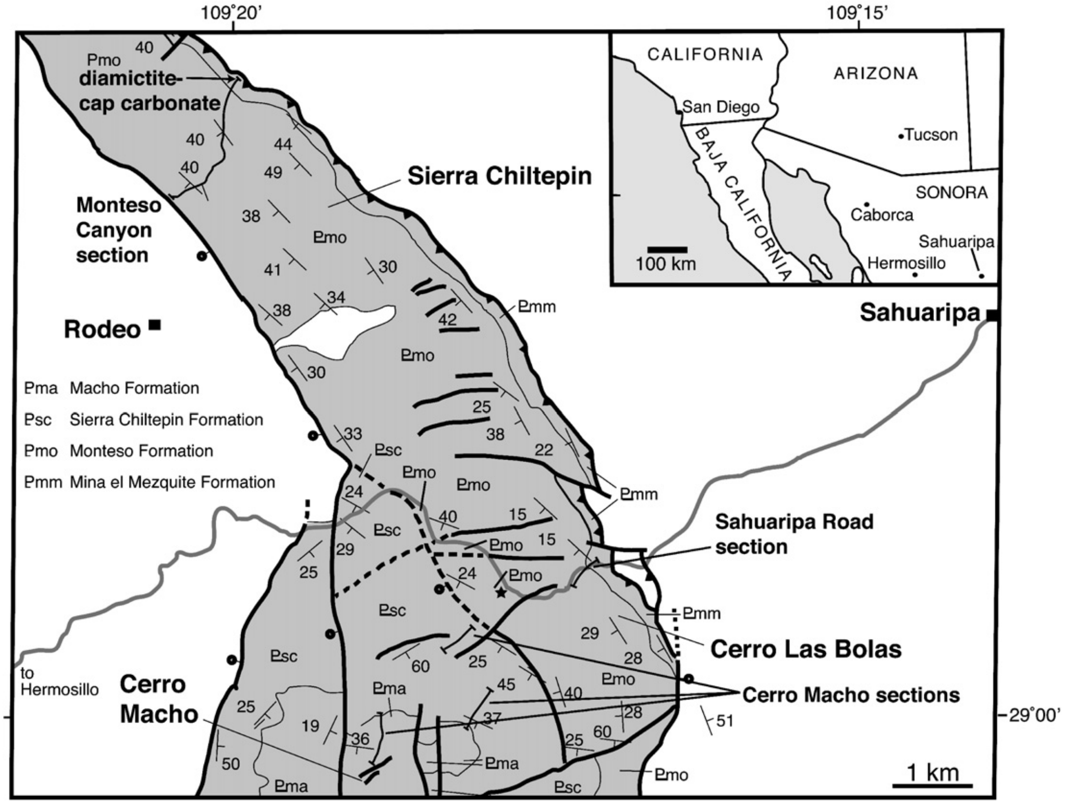

Fig. 1. Location and geologic map for the Sahuaripa area, after Stewart et al. (2002). The shaded area represents the Cerro Las Bolas Group. The stratigraphic sections discussed in the text are shown. The diamictite-cap carbonate units crop out at the northeastern end of Monteso Canyon and were not noted elsewhere in the region.

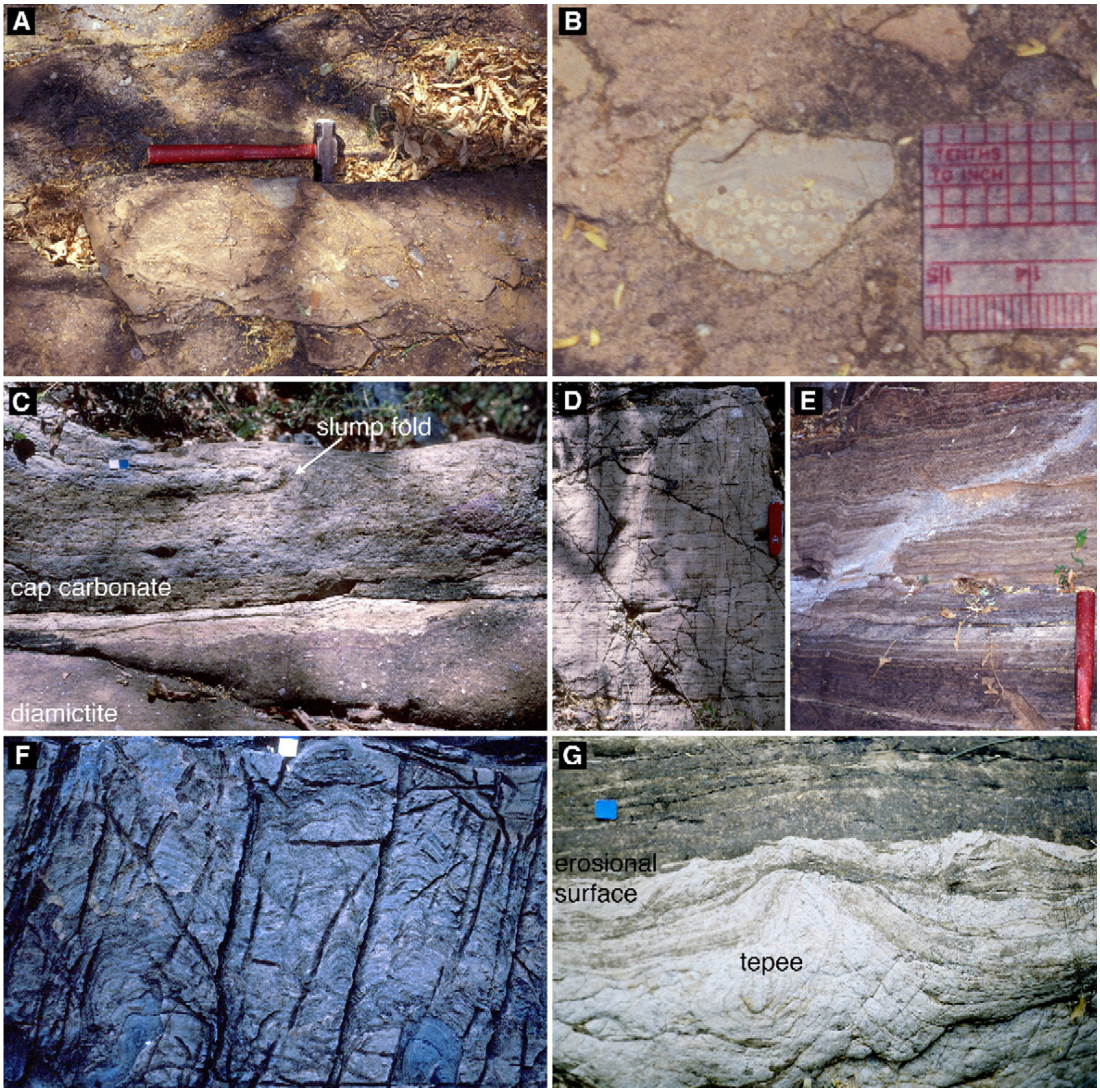

Fig. 2. Lithologic characteristics of the Cerro Las Bolas Group. Many exposures are shrouded by dense forest canopy; thus field photographs A and C–E have shadows of branches crossing rock surfaces. A) Diamictite at the base of the section. B) Carbonate clast in diamictite with pisoids commonly known as "giant ooids". Such clasts compare well with similar clasts in the Surprise Member of the Kingston Peak Formation in Death Valley (Corsetti and Kaufman, 2003). C) The contact between the diamictite (below) and the cap carbonate. A slump fold is apparent in the basal part of the cap carbonate (cf. Rodrigues-Nogueira et al., 2003). D) The basal 5 m of the cap carbonate is well-indurated. E) The remaining Mina el Mezquite Formation consists of finely laminated calcareous siltstones and shales. F) Stromatolites from the Monteso Formation. The finely laminated branching stromatolites are present but somewhat obscured by the regional vertical jointing pattern. G) Contact between supratidal carbonates with tepee structures (below) and subtidal carbonates above (likely parasequence boundary) in the upper part of the Monteso Formation.

et al., 1984). In fact, certain aspects of the stratigraphy are so similar to each other that some hypothesize that the Caborca succession was part of the Death Valley succession and was displaced as much as 800 km to the south along the Mojave–Sonora megashear, a cryptic left-lateral structure of disputed age (likely Jurassic) (Anderson and Silver, 1979; Stewart et al., 1984; Iriondo et al., 2004). No glacial deposits are currently known from the Caborca succession. If the absence of glacial deposits is not an artifact of subsequent erosion or initial non-deposition, we would consider the Caborca succession to be younger than the last Neoproterozoic glacial interval. Additional Neoproterozoic strata occur to the southeast of the Caborca succession (Stewart and Poole, 2002), but their lithostratigraphic correlatives within Sonora and to the north are less clear. Strata of the El

Aguila Group (considered younger than the 1.1 Ga detrital zircons it contains) and the Las Viboras Group (considered younger than the 1.057 Ga detrital zircons it contains) are particularly enigmatic (Stewart et al., 2002). Stewart et al. (2002) consider them to be older than miogeoclinal strata; they also lack glacial deposits. We hypothesize that the El Aguila Group and the Las Viboras Group were deposited between ~1000 Ma and ~750 Ma, assuming as above, that the absence of glacial deposits is not related to contemporaneous non-deposition or succeeding erosion. The Cerro Las Bolas Group occurs west of Sahuaripa in eastern Sonora near the border with Chihuahua, Mexico (Stewart et al., 2002) (Fig. 1) and contains a significant and well-preserved succession of Neoproterozoic strata, including a mixed carbonate-siliciclastic succession amenable to integrated chemostratigraphic and lithostratigraphic analysis.

3. Cerro Las Bolas Group

The Cerro Las Bolas Group (Stewart et al., 2002) is exposed in southeastern Sonora near the town of Sahuaripa and consists of ~2600 m of mixed siliciclastic-carbonate strata with a thin but significant diamictite unit at its base (Fig. 1). Dense vegetation and rugged topography limit access to the succession; our study was primarily conducted in the Sierra Chiltepín and Cerro El Carrizo (Cerro Macho) area to the west of Sahuaripa, Sonora, Mexico. In this region, the succession is in thrust contact with Cretaceous rocks and was once considered Cretaceous or Carboniferous by previous workers (see Stewart et al., 2002 and references therein). The units exposed in the area include the Mina el Mezquite Formation, Monteso Formation, Sierra Chiltepín Formation, and Macho Formation. We have adopted the formational, member, and numerical sub-unit terminology in Stewart et al. (2002) for our stratigraphic columns ("unit" designation on our stratigraphic columns correspond to the detailed unit descriptions in Stewart et al., 2002). A more detailed stratigraphic description of the units can be found in Stewart et al. (2002). The Cerro Las Bolas Group contains 1.1 Ga zircons (discussed below) that provide a maximum depositional age (Stewart et al., 2002).

The base of the Cerro Las Bolas Group consists of a 20 m thick unnamed diamictite (unit 1 of Stewart et al., 2002) previously unrecognized in the region in thrust contact with Cretaceous rocks below. Diamictite clasts are matrix-supported, poorly sorted, rounded to angular, and heterolithic, including outsized granitic, volcanic, and carbonate clasts floating in a brown, carbonate-rich muddy matrix (Fig. 2A). The color of the matrix may indicate that it is iron-rich. Of particular note, at least one grey dolostone clast composed of pisoids (giant ooids) typical of Neoproterozoic successions elsewhere was found in the diamictite (Fig. 2B). The source for the clasts is unknown, as the diamictite unit forms the base of the Neoproterozoic section in the Sierra Chiltepín area. However, it is interesting to note that the older of two glacial diamictites exposed in the Death Valley area also contains abundant carbonate debris, including clasts with similar pisoids sourced from the underlying Beck Spring Dolomite (Corsetti and Kaufman, 2003). The upper 20 cm of the diamictite unit is laminated and the laminae are deformed around outsized clasts.

The diamictite is sharply overlain by a grey finely-laminated, well-indurated, 5 m thick dolomitic mudstone (base of unit 2 of Stewart et al., 2002) that comprises the base of the Mina el Mezquite Formation (Fig. 2C–D). The laminated dolostone contains small soft sediment folds near the contact with the diamictite (Fig. 2C). The unit is overlain by a somewhat less-resistant red and grey colored, finely-laminated platy to flaggy splitting, rhythmically-bedded, dolostone, silty limestone and limey siltstone unit (Fig. 2E). Much of this unit is covered in Monteso Canyon and is more easily observed on the northeast flank of Cerro Macho. The upper part of the Mina el Mezquite Formation contains two prominent yellow-grey limestone units interbedded with limey siltstone.

The Monteso Formation conformably overlies the Mina el Mezquite Formation, is well-exposed in Monteso Canyon, and consists of parallel-laminated to cross-stratified dolostone packstones and grainstones punctuated by the siliciclastic Sahuaripa Member (quartzite, unit 8), Rodeo Member (quartzite, unit 14) and a thin quartz conglomerate (unit 18). Intraformational conglomerates, mud cracks, and tepee structures are common in the Monteso Formation. Small columnar branching stromatolites (~5 cm wide and 20 cm tall) are abundant in unit 12 (Fig. 2F). Unfossiliferous bedded black cherts, nodules and lenses are prominent in the dolostones of the upper Monteso Formation, and a distinctive meter-scale channel occurs in the middle of unit 22.

Sedimentary structures indicate that the Monteso Formation represents shallower paleoenvironments than the underlying Mina el Mezquite Formation (Stewart et al., 2002). The quartzites are likely shallow marine and/or fluvial and the conglomerates are likely fluvial and may represent channel fills. Many of the dolostone units record meter-scale shallowing upward successions (akin to parasequences characterized by subtidal overlain by inter- or supratidal facies) typical of shallow carbonate platform deposition (Fig. 2G). The underlying

Mina el Mezquite Formation and the lower part of the Monteso Formation (to unit 13) form one large scale shallowing upward succession. The conglomerate units broadly divide the Monteso Formation into several smaller scale disconformity-bounded shallowing upward successions. Limited outcrop precluded tracing the presumed stratigraphic breaks laterally for more detailed sequence stratigraphic analysis. Detrital zircons from the Sahuaripa Member have a minimum age of ~1.1 Ga (Stewart et al., 2001), thus providing a maximum age for this part of the succession and indicating that the glacial units are not associated with the Paleoproterozoic glacial episodes (e.g., Kirschvink et al., 2000). A sill was sampled from the succession, but it yielded a Mesozoic age (Stewart et al., 2002).

Quartz pebble conglomerates of the basal Sierra Chiltepín Formation (unit 26) are in abrupt contact with the underlying Monteso Formation and mark a change from carbonate-dominated to intimately mixed siliciclastic-carbonate deposition. The lower half of the formation is predominantly siliciclastic, contains conglomerate, sandstone, and siltstone, and is poorly-exposed. The remaining units form siliciclastic-carbonate couplets. An idealized Sierra Chiltepín Formation couplet is approximately 100 m thick and contains quartzite/conglomerate at its base, siltstone and/or calcareous siltstone and sandstone in the middle, and is capped by carbonate beds; the overall siliciclastic component of the couplet is ~75% and the carbonate component is ~25%. The carbonate units (both limestone and dolostone) are sandy and generally contain shallow water indicators, including intraformational conglomerates and polygonal upturned mud cracks. Detrital zircons from the quartzites in the lower part of the formation also have a minimum age of ~1.1 Ga (Stewart et al., 2001) and thus constrain the unit to have been deposited subsequent to 1.1 Ga.

The Macho Formation is relatively resistant and forms the top of the Neoproterozoic succession near Sahuaripa. The contact with the underlying Sierra Chiltepín Formation is poorly exposed. In general, the Macho Formation is composed of cross-bedded sandy dolostone to dolomitic sandstone and becomes less carbonate rich towards the top. Some of the sandy dolostones are peloidal, and nearly all of the carbonates in the Macho Formation contain a significant amount of well-rounded quartz sand.

4. δ^{13}C chemostratigraphy

Carbonates of the Cerro Las Bolas Group were sampled for δ^{13}C in order to better constrain the age of the succession. Based on detrital zircons, the Cerro Las Bolas Group is younger than ~1.1 Ga. The absence of metazoan body or trace fossils within abundant well-preserved subtidal siliciclastic and carbonate facies, and the presence of the distinctive diamictite-carbonate couplet at the base of the succession suggests a Neoproterozoic rather than Phanerozoic age. Post-750 Ma Neoproterozoic successions are characterized by very large carbon isotopic fluctuations, with positive δ^{13}C excursions to +12‰ and negative excursions to −11‰ noted worldwide (e.g., Knoll, 2000; Walter et al., 2000). Such massive isotopic changes are nearly unprecedented in geologic history and thus may provide a means for correlation in poorly fossiliferous successions.

Interpreting the secular trends in isotope abundances requires that primary isotope compositions are preserved in such ancient rocks. We employed the techniques outlined in Kaufman and Knoll (1995) in order to evaluate our samples for diagenetic overprinting. A thin and thick section pair was made from each sample. The thin section was petrographically evaluated for diagenetic alteration, water/rock interaction, and paleoenvironmental information. The thick section was photographed under cathodoluminescence (a technique that highlights post-depositional alteration) and further evaluated for alteration. The least altered primary marine phases were microdrilled from the thick section based on the previous evaluation and analyzed for δ^{13}C. Carbonate powders were reacted for 10 min. at 90 °C with anhydrous H_3PO_4 with a Multiprep inlet system in-line connected to a dual inlet Isoprime gas source mass spectrometer in the Stable Isotope Facility of the University of Maryland Geochemical Laboratories. Isotopic results are expressed in the standard δ notation as per mil (‰) deviations from the V-PDB international standard. Uncertainties determined by multiple measurements of a laboratory standard carbonate (calibrated to NBS-19) during each run of samples were better than 0.05‰ for both C and O isotopes. The δ^{18}O values from each sample were used to evaluate the amount of water–rock interaction and post-depositional alteration.

Petrographically screened microsamples with δ^{18}O greater than −10‰ were considered adequately preserved (Kaufman and Knoll, 1995). In general, the δ^{18}O is ~−10‰ or greater for the lower part of the Mina el Mezquite Formation (average: −8.9‰), the Monteso Formation (average: −7.5‰), and the Macho Formation (average: −3.8‰) (Table 1). The upper part of the Mina el Mezquite Formation (unit 5, average: −13.2‰) and the Sierra Chiltepín Formation (average: −10.7‰) have some δ^{18}O values lighter than −10‰ and are thus

Table 1
$\delta^{13}C$ and $\delta^{18}O$ for the Monteso Canyon, Sahuaripa Road, and Cerro Macho sections

Monteso Canyon section

Sample number	$\delta^{13}C$	$\delta^{18}O$	Meters above base of first carbonate
MC-1	−3.1	−9.5	0
MC-2	−3.2	−8.7	1
MC-3	−2.9	−9.1	2
MC-4	−2.7	−9.2	3
MC-5	−3.1	−8.5	4
MC-6	−3.4	−12.1	24
MC-7	−3.4	−13.2	37
MC-8	−4.3	−14.1	56
MC-9	−4.3	−13.3	97
MC-10	−5.3	−11.8	128
MC-11	−4.5	−10.7	151
MC-12	−3.5	−4.9	163
MC-13	−2.6	−4.1	179
MC-14	−1.5	−5.9	198
MC-15	−2.8	−5.2	218
MC-16	−5.0	−12.1	235
MC-17	−1.5	−6.0	254
MC-19	−2.4	−6.0	269
MC-20	−2.1	−5.0	291
MC-21	−0.8	−7.0	311
MC-22	−1.2	−6.7	327
MC-23	−0.2	−8.3	339
MC-24	0.4	−6.8	355
MC-25	0.0	−6.0	369
MC-26	0.3	−7.2	381
MC-27	0.2	−6.9	399
MC-28	1.6	−6.0	407
MC-29	2.6	−8.1	415
MC-31	7.1	−7.6	515
MC-32	6.6	−6.8	526
MC-33	8.2	−6.9	533
MC-35	7.4	−4.2	546
MC-36	9.7	−7.8	556
MC-37	8.0	−7.2	575
MC-38	7.5	−5.6	590
MC-39	7.0	−6.8	606
MC-40	6.7	−8.0	616
MC-41	1.6	−9.8	654
MC-42	3.9	−9.4	663
MC-43	2.7	−10.3	679
MC-44	0.6	−9.7	688
MC-45	1.7	−10.2	698
MC-46	1.9	−9.4	713
MC-47	2.0	−12.6	732
MC-48	1.6	−9.1	741
MC-49	3.0	−9.3	748
MC-50	3.4	−6.6	763
MC-51	2.9	−7.4	783
MC-52	2.2	−7.6	794
MC-53	0.8	−7.8	811
MC-54	1.5	−9.1	819
MC-57	5.1	−7.8	835
MC-58	5.5	−6.6	856
MC-59	4.7	−6.7	877
MC-60	4.5	−7.2	900
MC-61	4.1	−8.2	920
MC-62	6.7	−9.2	942
MC-63	8.3	−5.6	964
MC-64	5.5	−10.7	983

Table 1 (*continued*)

Sahuaripa Road section

Sample Number	$\delta^{13}C$	$\delta^{18}O$	Meters above base of section
CM-88	−4.2	−14.4	0
CM-90	−3.3	−15.7	38
CM-91	−1.7	−4.4	53
CM-93	−3.5	−4.6	63
CM-94	−5.2	−5.8	71
CM-95	−4.1	−5.4	85
CM-96	−3.9	−5.1	105
CM-97	−3.8	−5.6	122
CM-98	−4.5	−7.1	209
CM-99	−3.3	−4.5	221
CM-100	−1.2	−5.0	251
CM-101	−1.2	−4.6	266
CM-102	−2.5	−4.0	290
CM-103	−3.4	−5.4	308
CM-104a	−0.6	−4.9	316
CM-104b	−0.5	−5.7	325
CM-105	0.5	−5.1	330
CM-106	1.1	−4.4	334
CM-107	0.2	−5.2	340
CM-108	1.3	−4.7	346
CM-109	1.9	−4.9	349
CM-110	2.8	−1.0	355
CM-111	2.9	−4.3	357
CM-112	2.2	−3.0	360
CM-114	1.0	−5.1	366
CM-115	3.3	−4.8	370
CM-116	1.3	−3.7	377

Cerro Macho section

Sample number	$\delta^{13}C$	$\delta^{18}O$	Meters above base of section
MC-65	−2.5	−7.5	306
MC-66	−2.3	−9.7	434
MC-67	2.2	−12.6	482
MC-68	2.8	−6.7	550
MC-69	2.4	−10.8	563
MC-70	2.9	−10.1	650
MC-71	3.8	−12.6	656
MC-72	3.6	−14.6	661
MC-73	4.0	−11.3	669
MC-74	2.1	−13.6	745
MC-75	2.1	−8.2	750
MC-76	2.4	−9.5	758
MC-77	2.0	−7.8	765
MC-78	2.2	−8.9	830
MC-85	1.3	−10.1	835
MC-86	2.0	−9.5	840
MC-87	2.3	−12.3	845
MC-79	2.6	−8.6	853
MC-80	1.9	−11.5	1003
MC-81	2.3	−12.7	1010

Table 1 (*continued*)

Cerro Macho section			
Sample number	δ^{13}C	δ^{18}O	Meters above base of section
MC-82	2.1	−13.0	1018
MC-83	2.2	−13.3	1026
MC-84	1.0	−11.6	1084
M-1	−1.3	−3.9	1126
M-2	−0.5	−4.4	1158
M-3	−1.5	−1.8	1312
M-4	−0.6	−2.9	1333
M-5	−0.7	−4.5	1382
M-6	0.2	−2.1	1414
M-7	−1.5	−4.6	1450
M-8	−0.4	−5.6	1507
M-9	−0.7	−4.4	1569

considered less robust. Open symbols on the stratigraphic columns denote those samples in which we have the least confidence based on the criteria outlined above. A plot of δ^{18}O versus δ^{13}C exhibits no significant correlation and thus most of the samples are considered relatively well-preserved with respect to strata of similar age (Fig. 3).

The Cerro Las Bolas Group was sampled for δ^{13}C chemostratigraphy at three separate localities (Fig. 1). Each locality overlaps with at least one other locality in order to evaluate the lateral continuity of the δ^{13}C profiles. The Monteso Canyon section can be reached via an unimproved road to Rodeo (off the main Sahuaripa road), a primitive road to the mouth of Monteso Canyon, and by foot traverse up the canyon. The other two localities can be accessed via foot traverse from the Sahuaripa road. The Monteso Canyon section begins at the easternmost end of Monteso Canyon and contains the diamictite unit, the Mina el Mezquite Formation, and the Monteso Formation. The Sahuaripa Member (unit 8) is missing in this section, likely by faulting. The Sahuaripa Road section is on the northeast flank of Cerro Macho on the south side of the road from Sahuaripa and contains the upper portion of the Mina el Mezquite Formation and the lower part of the Monteso Formation, including both the Sahuaripa and Rodeo Members. Unit 13 of the Monteso Formation was also sampled at an additional site on the south side of the road due to better exposure. The Cerro Macho section was measured in three segments, is also located on the northeast flank of Cerro Macho, and consists of the relatively poorly exposed Sierra Chiltepín Formation and the resistant Macho Formation. (Table 1)

5. Monteso Canyon section

In general, the Mina el Mezquite Formation records negative δ^{13}C values between −5.3‰ and −2.7‰ (Fig. 4). The well-indurated 5 m thick finely laminated grey carbonate in sharp contact with the diamictite at the base of the section records a mildly rising trend, from −3.1‰ to −2.7‰. The overlying less-resistant red and grey colored rhythmically-bedded dolostones and silty limestones record slightly more negative δ^{13}C values, although many of them are considered less robust by our diagenetic screening procedure. The Monteso Formation records a prominent positive δ^{13}C excursion from −3.5‰ in unit 7 that culminates in highly positive values of +9.9‰ in the middle of unit 15. The excursion spans approximately 300 m of section (although the Sahuaripa Member is missing in this section). δ^{13}C values decline to +6.7‰ at the top of unit 15. δ^{13}C values decrease abruptly to 1.6‰ across the conglomerate and quartzite in unit 18 and begin another significant rise to 8.3‰ at the top of the Monteso Formation. The rise is not monotonic however, but rather displays several oscillations on the order of 2‰ in addition to an abrupt jump of approximately 4‰ within unit 22 across the aforementioned channel. Thus, it is likely that the channelization represents a stratigraphic break of significant duration.

6. Sahuaripa Road section

The upper portion of the Mina el Mezquite Formation (unit 5) records negative δ^{13}C values between −4.2‰

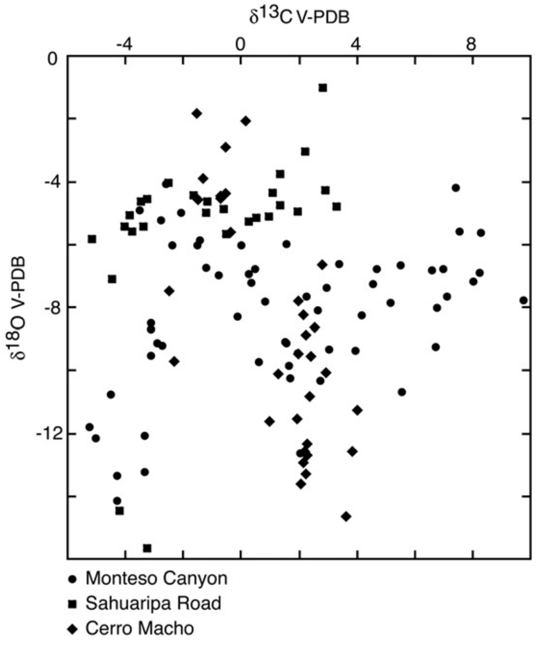

Fig. 3. Cross-plot between δ^{13}C and δ^{18}O. No obvious diagenetic trend is apparent in these data.

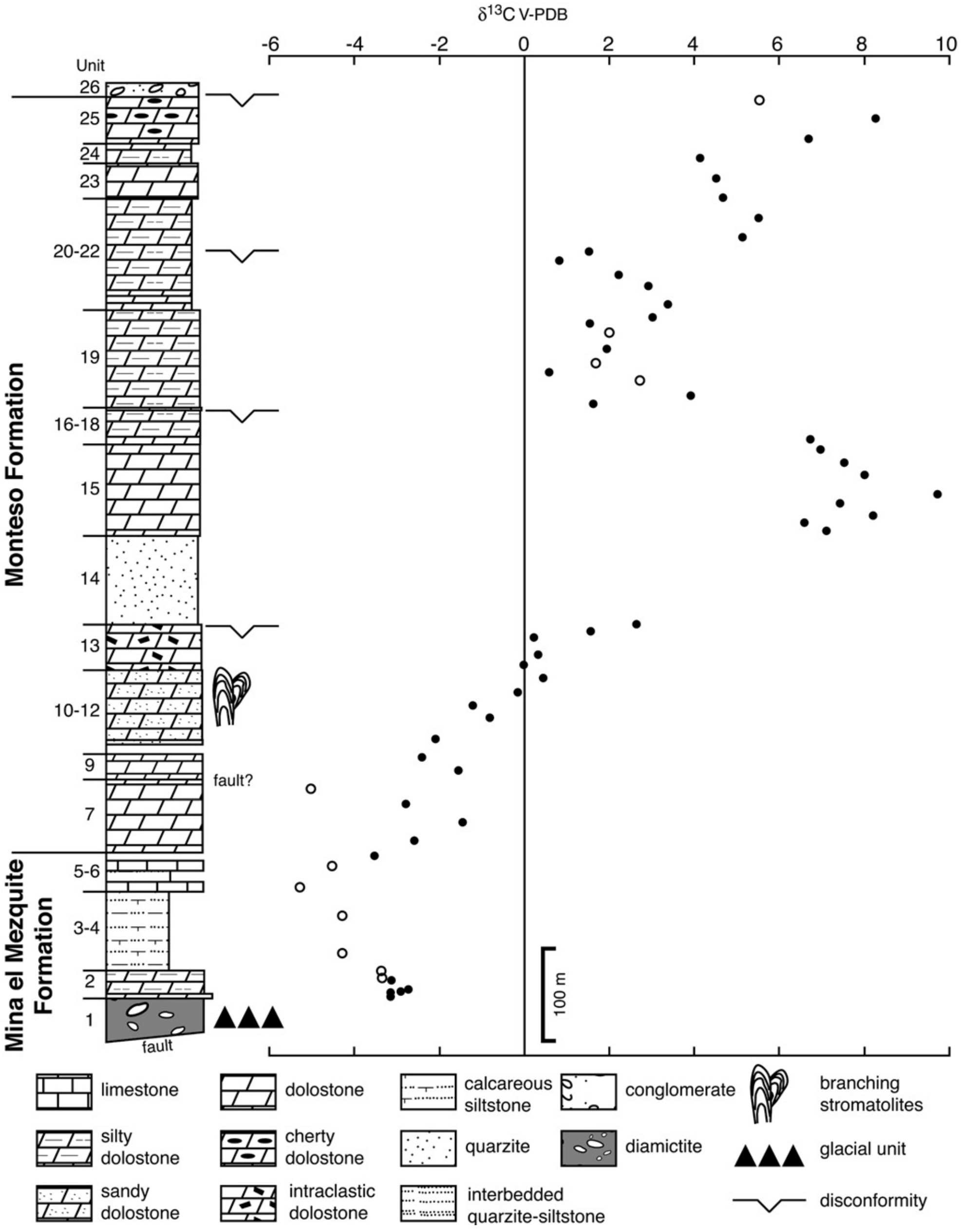

Fig. 4. Isotope stratigraphy of the Monteso Canyon section (Mina el Mezquite and Monteso Formations). Note that the Sahuaripa member (quartzite) is missing from this section, likely due to faulting. Filled symbols represent samples in which we have more confidence based on petrographic and geochemical screening; the symbols presented here are used throughout.

and −3.3‰, similar to those seen in Monteso Canyon (Fig. 5). However, the δ^{18}O of the unit 5 samples is quite depleted (between −14.4‰ and −15.7‰) and upper Mina el Mezquite values should be treated with caution. As in the Monteso Canyon section, a significant positive δ^{13}C excursion begins in the basal Monteso Formation and continues to a maximum at the top of unit 13 of +3.3‰ in this abbreviated section. Unit 13 was sampled at a much finer scale at this section and reveals a coherent positive δ^{13}C isotopic trend between 0.5‰ and 3.3‰, confirming the trend broadly noted in the Monteso Canyon section. The Sahuaripa Road section terminates at the Rodeo Member (unit 14), so the positive excursion noted in Monteso Canyon is not preserved here. It is notable that the difference in isotopic compositions below and above the Sahuaripa Member quartzite is

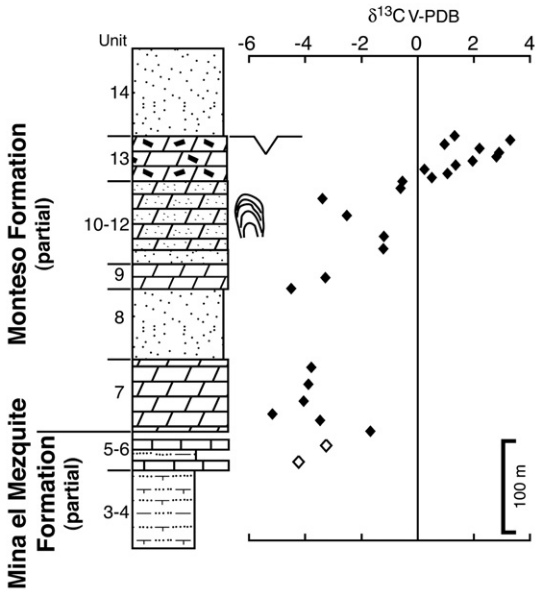

Fig. 5. Isotope stratigraphy of the Sahuaripa Road section (upper Mina el Mezquite and lower Monteso Formations).

minimal. We do not have a continuous isotopic record within the siliciclastic unit, but the isotopic similarities below and above might suggest little stratigraphic break across the interval (contrast with the δ^{13}C values below and above the quartz pebble conglomerate, unit 18, in the Monteso Canyon section).

7. Cerro Macho section

The basal Sierra Chiltepín Formation is predominantly siliciclastic and thus not appropriate for δ^{13}C chemostratigraphy (Fig. 6). Two sandy carbonate units in the siliciclastic rich interval record mildly negative δ^{13}C values, in contrast to the highly positive δ^{13}C values noted in the underlying Monteso Formation (there is a 7‰ difference between the uppermost Monteso Formation and the sporadic carbonate beds in the basal Sierra Chiltepín Formation). The remaining Sierra Chiltepín Formation records mildly positive δ^{13}C values between 1.0‰ and 4.0‰. Interestingly, each carbonate unit records a small-scale positive δ^{13}C excursion from bottom to top (i.e., units 41, 43, 45, and 47). Units 41 and 45 are particularly excellent examples of the small-scale phenomena: unit 41 records a coherent positive excursion from 2‰ to 4‰ and unit 45 records a similar excursion from 1‰ to 3‰. In contrast, the sandy dolostones of the overlying Macho Formation record mostly mildly negative δ^{13}C values between −1.3‰ and 0.2‰.

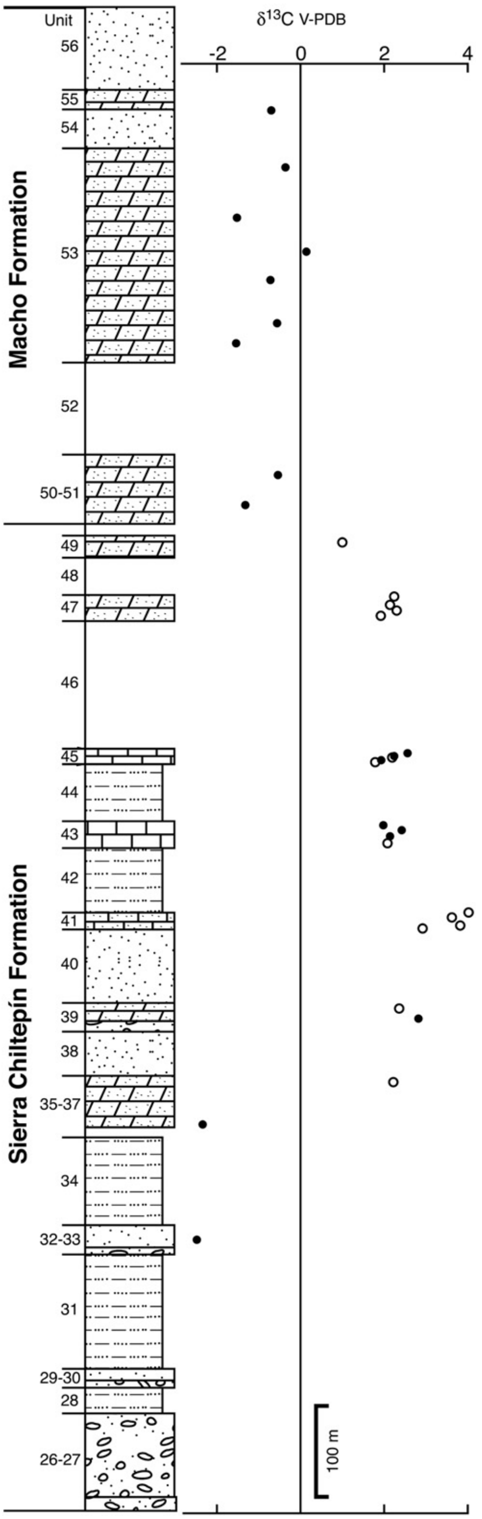

Fig. 6. Isotope stratigraphy of the Cerro Macho section (Sierra Chiltepín and Macho Formations). Note the siliciclastic-carbonate couplets within the Sierra Chiltepín Formation. Filled symbols represent samples in which we have more confidence based on petrographic and geochemical screening.

8. Discussion

Together with the lithologic features of the diamictite-cap carbonate, several aspects of the δ^{13}C profile for the Cerro Las Bolas Group are noteworthy, including the negative δ^{13}C values of the units directly above the basal diamictite and the fact that the δ^{13}C rise to highly positive values above the diamictite (Fig. 7). Integrated analysis of Neoproterozoic successions from a myriad of basins reveals that there were several glaciogenic events during this interval and that almost all of the putative glaciogenic strata are overlain by cap carbonates characterized by unusual chemistry, sedimentary structures, and/or microbialites (e.g., Kaufman et al., 1991; Kennedy, 1996; Kaufman, 1997; Kaufman et al., 1997; Hoffman et al., 1998a,b; Kennedy et al., 1998; Prave, 1999; James et al., 2001; Halverson et al., 2002; Hoffman and Schrag, 2002; Corsetti et al., 2003; Corsetti and Kaufman, 2003; Fraiser and Corsetti, 2003; Rodrigues-Nogueira et al., 2003). For example, Neoproterozoic cap carbonates record pronounced negative δ^{13}C excursions in contrast to the highly positive δ^{13}C values that characterize much of Neoproterozoic time (Kaufman et al., 1997; Kennedy et al., 1998). Many of them are composed of a finely laminated basal cap dolostone (some with subaqueous tepee-like structures) followed by additional dolostone or limestone that may include relatively unusual carbonate fabrics, including seafloor-precipitated fans, rollup structures, and seafloor-precipitated barite fans (e.g., Kennedy, 1996; James et al., 2001; Hoffman and Schrag, 2002; Allen and Hoffman, 2005).

The glacial-cap carbonate couplet has been identified elsewhere in western North America from Death Valley in California north to the Mackenzie Mountains in Canada, but until now, had not been recognized in Sonora. We feel relatively confident that the diamictite-cap dolostone pattern is in fact repeated in the basal Cerro Las Bolas Group, based on the stratigraphic pattern (diamictite-cap carbonate) and δ^{13}C isotopic signature (negative δ^{13}C values in the cap carbonate rising to positive values in overlying strata). Interestingly, the Cerro Las Bolas diamictite contains carbonate clasts with pisoids similar to those found as clasts in the older of two glacial diamictites in the Kingston Peak Formation of Death Valley (and sourced from the underlying Beck Spring Dolomite; Corsetti and Kaufman, 2003). It should be stated that we do not have overly robust evidence for the glacial origin of the Cerro Las Bolas Group diamictite (e.g., striated clasts, unambiguous dropstones, etc.), as the laminae in the upper 20 cm of the diamictite unit were deflected around outsized clasts during compaction rather than just below them in classic dropstone arrangement. It is possible that the diamictite has a non-glacial origin. However, the glacial-cap carbonate progression in this succession is so similar to those from elsewhere around the world, and the color of the diamictite matrix implies iron-enrichment, that we postulate the diamictite to be glaciogenic. If this hypothesis is correct, this succession represents the only known occurrence of a Neoproterozoic diamictite-cap carbonate pair in Mexico, despite the widespread occurrence (Stewart et al., 2002) of many well-preserved km-thick exposures of Neoproterozoic strata in Sonora.

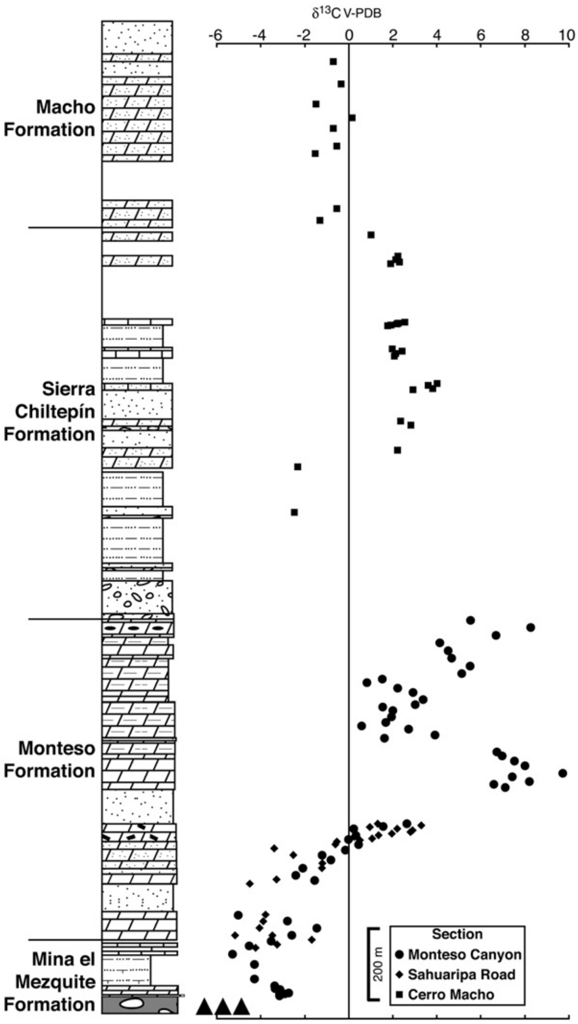

Fig. 7. Composite isotope stratigraphy for the Cerro Las Bolas Group. Note the clear overlap in isotopic profiles between each section (i.e., little alteration between sections). The cap carbonate records negative δ^{13}C values and the overlying Monteso Formation records the isotopic maximum of ~+10‰ suggesting the diamictite at the base of the section belongs to the older (Sturtian) glacial episode.

Identification of a diamictite-cap carbonate succession in eastern Sonora, coupled with the detrital zircon data, supports a Neoproterozoic age assignment for the Cerro Las Bolas Group, and constrains the age of the group to between ~758 to ~580 Ma, the age of the maximum and minimum ages for well-dated glacial-cap carbonate units found elsewhere (Fig. 8). However, it may be possible to constrain the age even further if we examine some of the details recorded in the succession.

It is widely believed that there were at least three great "ice ages" in Neoproterozoic time, an older interval ca. 750–700 (Brasier et al., 2000; Allen et al., 2002; Fanning and Link, 2004; Zhou et al., 2004), a middle interval ca. 635 Ma (Hoffmann et al., 2004), and a younger interval ca. 580 Ma (Bowring et al., 2003; Calver et al., 2004) (Fig. 8). Names have been applied to the glacial intervals: the older is commonly termed the Sturtian, the middle the Marinoan, and the youngest the Gaskiers, each based on a key locality. However, the actual correlation between the key localities is currently debated (e.g., Calver et al., 2004), so we caution the use of the informal names until the correlations can be strengthened. We will use them here as they have been used in the recent literature, but care is again suggested. Some suggest that there may have been more glacial episodes during this time (e.g., Kaufman et al., 1997; Knoll, 2000), and recent dates and lithostratigraphy from Idaho (Lund et al., 2003; Fanning and Link, 2004; Lorentz et al., 2004) suggest the possibility of a fourth ice age between the classic Sturtian and the Marinoan

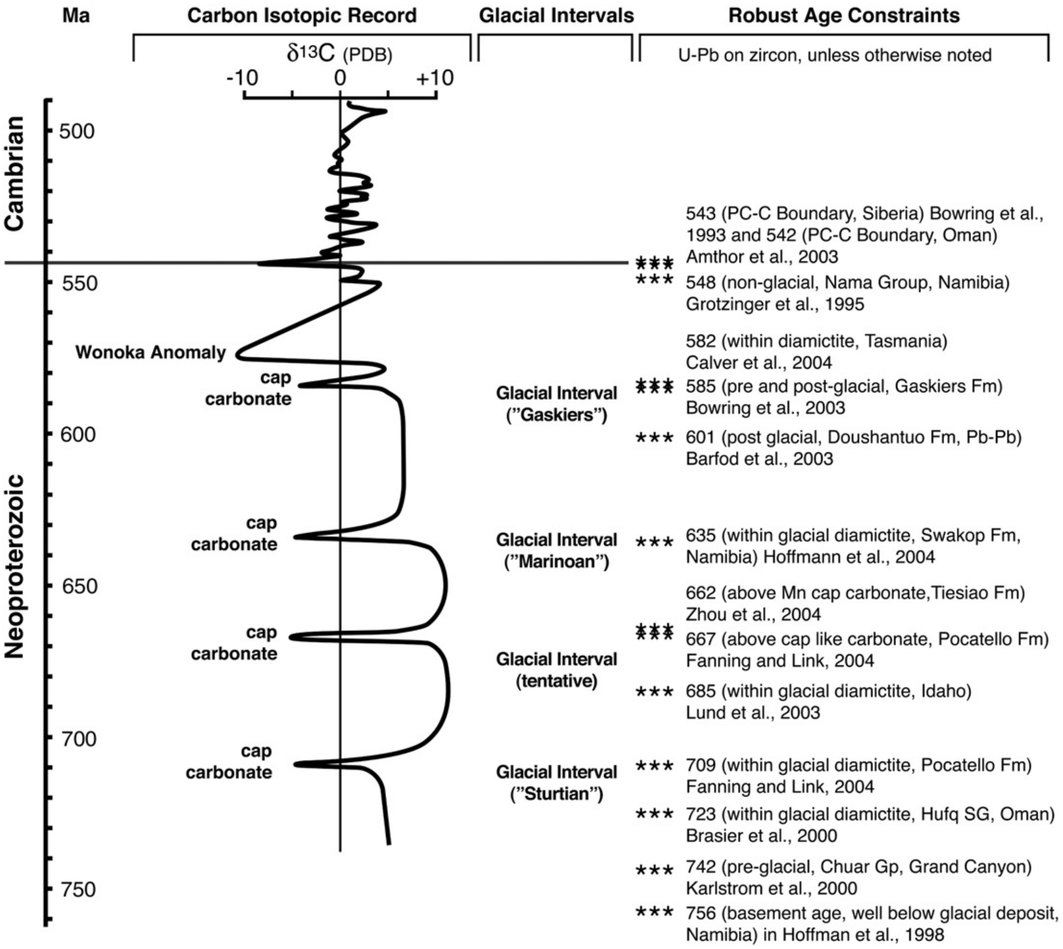

Fig. 8. Simplified summary of δ^{13}C stratigraphy for the Neoproterozoic–Cambrian based on radiometrically-calibrated successions (Bowring et al., 1993; Grotzinger et al., 1995; Hoffman et al., 1998b; Brasier et al., 2000; Karlstrom et al., 2000; Allen et al., 2002; Barfod et al., 2002; Halverson et al., 2002; Amthor et al., 2003; Bowring et al., 2003; Lund et al., 2003; Calver et al., 2004; Fanning and Link, 2004; Hoffmann et al., 2004; Lorentz et al., 2004; Zhou et al., 2004). The position of the Wonoka (Shuram) Anomaly is uncertain (see Kaufman et al., 2006-this volume). Condon et al. (2005) suggest it is younger than shown here. If incised valleys in the Johnnie Formation, Death Valley region, are related to Gaskiers glaciation (see discussion in Clapham and Corsetti, 2005), then it could predate the Gaskiers glaciation.

(Fanning and Link, 2004, consider the deposits as a phase of the Sturtian glaciaion) (Fig. 8). Kaufman et al. (1997) and Knoll (2000) examined many Neoproterozoic $\delta^{13}C$ profiles from around the world and determined that marine carbonates deposited during the interval between the Sturtian and Marinoan ice ages record some of the most enriched $\delta^{13}C$ values in geologic history (many basins around the world record $\delta^{13}C$ in excess of +8‰). The magnitude of isotopic change between the last cap carbonate atop the older Sturtian glacial deposits and the post-glacial strata approaches +18‰ in some cases. They envision a "biogeochemical divide" of unusually enriched $\delta^{13}C$ between the two ice ages. If this is the case, then the Cerro Las Bolas diamictite-cap carbonate belongs to the older ice age because the post diamictite $\delta^{13}C$ values reach ~+10‰ in the overlying Monteso Formation.

Some workers have noted textural differences between cap carbonates belonging to different ice ages and proposed that the identification of such features might also be useful for determining the age of the units (e.g., Kennedy et al., 1998; Hoffman and Schrag, 2002). These authors suggest that 'Sturtian' cap carbonates are dark colored, may contain microbial rollup structures, and record a rapid return to positive $\delta^{13}C$ values. In contrast, they suggest that 'Marinoan' cap carbonates record a $\delta^{13}C$ isotopic decline up-section, are predominantly pink in color and may contain sheet-crack cements, tubestones, and/or seafloor fans. Notably, the Cerro Las Bolas diamictite and the Mina el Mezquite cap carbonate contain aspects of both types of cap carbonates. For example, the thin finely laminated dark-colored cap dolostone (base of unit 2) records a mildly positive shift from −3.1‰ to −2.6‰ but never attains positive $\delta^{13}C$ values, and contains soft sediment deformation reminiscent of microbial rollups but not in the classic sense of a rollup with multiple rolled-up layers (Simonson and Carney, 1999; Grotzinger and James, 2000). Therefore, the cap dolostone at the base of unit 2 is more similar to Sturtian examples. The dolostone and limestone units that directly overly the cap dolostone, however, are red and grey colored and record more negative $\delta^{13}C$ values than the thin cap dolostone below, not unlike certain Marinoan cap carbonates, and the negative $\delta^{13}C$ values persist for over 100 m. No distinctive sedimentary structures, such as seafloor fans or sheet-cracks, were noted in this unit. Thus, lithologic criteria are absent, and the most compelling evidence is geochemical — overlying strata attain highly enriched $\delta^{13}C$ compositions, suggesting that the Cerro Las Bolas diamictite-cap carbonate is most consistent with a Sturtian age.

9. Small-scale rhythmic $\delta^{13}C$ excursions in the Sierra Chiltepin Formation

The Sierra Chiltepín Formation contains at least four siliciclastic-carbonate cycles interpreted to represent shallowing upward successions (Fig. 6). The average $\delta^{13}C$ value for this interval is ~2.5‰, but each carbonate unit records a small, generally 2‰ positive excursion about the mean value. It is possible that the small-scale excursions simply represent small-scale secular variation in the $\delta^{13}C$ of seawater, or a slight diagenetic overprint associated with shallowing. An alternative view is also viable, albeit speculative. It is possible that a paleoenvironmental bias is recorded within each cycle — implying that an onshore–offshore ^{13}C gradient was present during deposition. Thus, the deeper paleoenvironments record slightly more depleted $\delta^{13}C$ values than the shallower ones. However, the inferred water depth between the base and the top of the carbonate units, although not well constrained, is thought to be relatively small. Therefore, the carbon isotopic gradient may have been relatively steep compared to the modern ocean. The presence of such a gradient is consistent with recent interpretations that the Neoproterozoic carbon cycle was dominated by a vast pool of dissolved organic matter which would foster a steep ^{13}C depth gradient (Rothman et al., 2003).

10. The utility of $\delta^{13}C$ stratigraphy for correlating Neoproterozoic successions

The Cerro las Bolas Group is a typical Neoproterozoic succession in that it contains a diamictite-cap carbonate couplet with a correspondingly negative $\delta^{13}C$ signature, it lacks useful biostratigraphic information (i.e., acritarchs, microbiotas, Ediacaran-type body fossils, and trace fossils), it is nearly devoid of datable igneous units or post-1.1 Ga detrital zicons, and it records a high amplitude oscillatory $\delta^{13}C$ profile (Fig. 8). Future $^{87}Sr/^{86}Sr$ chemostratigraphy may be useful, but the succession is mostly dolostone, which is problematic for the preservation of strontium isotope signatures. The limestones that are preserved do not pass our diagenetic screening. We hypothesize a "Sturtian" age for the diamictite-cap carbonate based on the current understanding of Neoproterozoic $\delta^{13}C$ stratigraphy, but this interpretation is based on generalizations that fit the global pattern as we presently understand it. The remaining Cerro Las Bolas Group, above the highly enriched $\delta^{13}C$ values in the Monteso Formation, is essentially devoid of useful chronostratigraphic information. Therefore, these $\delta^{13}C$-based correlations should be viewed as hypotheses to guide further testing. In the absence of further field mapping and reconnaissance in the Sahuaripa region, it is not immediately clear what additional tests would strengthen such correlations. In this way, the Cerro Las Bolas Group is typical of most Neoproterozoic successions around the world.

11. Conclusion

The basal Cerro Las Bolas Group near Sahuaripa, eastern Sonora, Mexico contains a diamictite-cap carbonate couplet characteristic of Neoproterozoic successions around the world and is the first such succession reported from Mexico. The cap carbonate at the base of the Mina el Mezquite Formation records a negative $\delta^{13}C$ anomaly and the $\delta^{13}C$ profile reaches $\sim+10‰$ in the overlying Monteso Formation. We preliminarily interpret the diamictite-cap carbonate succession to be Sturtian in age, ca. 750–700 Ma based on its position below strata characterized by highly positive $\delta^{13}C$ values. The discovery of this diamictite-cap carbonate succession furthers our understanding of Sonoran Neoproterozoic Earth history and adds to the growing database on Neoproterozoic isotope stratigraphy.

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