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- By a pressure of 4.2 GPa, after the *s*-to-*d* transition has begun, Cs collapses in volume by a factor of 3 and undergoes a phase transition from a close-packed structure to an open, body-centered tetragonal crystal structure [Cs(IV)] as a result of the more covalent, directional nature of the bonding involving large *d* orbitals (4). Cesium also becomes a superconductor at this pressure [J. Wittig, *Phys. Rev. Lett.* **24**, 812 (1970)]. *d* electrons have little electron density at the nucleus and, unlike other transition metals, Cs(IV) has no valence *s* electrons. As a result, the bonding in Cs(IV) is unusual, with minimal valence electron density at the nucleus and maximum electron density between the atoms. This hypothesis is confirmed by electronic structure calculations that show that Cs(IV) can be considered an electride, consisting of Cs<sup>+</sup> ions and interstitial electrons [H. G. von Schnering and R. Nesper, *Angew. Chem. Int. Ed. Engl.* **26**, 1059 (1987)]. The other heavy alkali metals, K and Rb, also exhibit large changes in electronic structure and bonding under pressure (1).
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- The charge density at the Wigner-Seitz radius can be determined from  $n_{WS} = 0.82 (K/V_m)^{1/2}$ , where *K* and *V<sub>m</sub>* are the bulk modulus (in gigapascals) and molar volume (in cubic centimeters), respectively, at a given pressure (12). Because the Miedema charge density parameters are adjusted empirically from experimental values (12), we estimated the charge densities at high pressure by adding a shift in charge density under pressure determined from this equation to the Miedema value at ambient pressure.
- Use of a single-crystal sapphire, which has great thermal and chemical stability, greatly retards or eliminates reaction between transition metals and the insulating medium in laser-heating experiments [G. Shen, P. Lazor, S. K. Saxena, *Phys. Chem. Minerals* **20**, 91 (1993); R. Boehler, *Nature* **363**, 534 (1993)]. Reaction between elemental K and clean sapphire plates can also be ruled out on thermodynamic grounds.
- Because K is very reactive, we took care to avoid introduction of water and oxygen impurities. Samples were loaded in a Vacuum Atmospheres glove box with a very high purity Ar atmosphere (~1 to 2 ppm O<sub>2</sub>-H<sub>2</sub>O). Before loading, the diamond cell, gasket, and sapphire crystals were heated to drive off any water or other adsorbed contaminants, then quickly loaded into the glove box while hot.
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- Other, much weaker diffraction lines were also observed, indicating the presence of a small amount of at least one more phase. The diffraction lines of Ni became weaker after laser heating but did not disappear. The presence of three phases violates the phase rule, indicating that thermodynamic equilibrium was not achieved. Equilibrium was not achieved because there were temperature gradients in the laser-heated sample, which arise because of the large thermal conductivity of the diamonds. Laser heating of the sample simultaneously from both sides would allow thermodynamic equilibrium to be reached.
- It is reasonable to expect that the large changes that occur in the size and electronic structure of the alkali metals under pressure will affect their behavior in other interesting or important chemical systems. For example, thermodynamic calculations indicate that formation of the compound CsF<sub>2</sub>, which would involve bonding to electrons in a noble gas configuration octet, should be favored under high pressure (J. V. Badding, unpublished data). The availability of the *d*-electron bonding state of the alkali metals should also allow new chemistry with many of the nonmetallic elements.
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## Detrital Zircon Link Between Headwaters and Terminus of the Upper Triassic Chinle-Dockum Paleoriver System

N. R. Riggs, T. M. Lehman, G. E. Gehrels, W. R. Dickinson

New detrital-zircon geochronologic data reveal that a through-going paleoriver connected Texas with Nevada in Late Triassic time. Sandstone from the Upper Triassic Santa Rosa Sandstone (Dockum Group) from northwestern Texas contains a detrital zircon suite nearly identical to that found in western Nevada in the Upper Triassic Osobb Formation (Auld Lang Syne Group, correlative with the Chinle Formation). The Santa Rosa Sandstone was derived in large part from the eroded Cambrian core of the Amarillo-Wichita uplift, as evidenced by abundant zircons with ages of 515 to 525 million years. Other zircon grains in the sandstone are Permian, Devonian, Proterozoic, and Archean in age and, with the exception of the Archean grain, are also matched by the population in the Nevada strata.

The sources and paths of ancient river systems are generally traced by distinctive grains (1), paleocurrents, and facies correlations, but these arguments provide no unique ties between source areas and sites of deposition. Distinctive clasts have been used with some success (2), but are of use only where coarse gravelly detritus is preserved. It remains uncertain whether an ancient river can be traced successfully from headwaters to terminus by such potentially ambiguous means.

The Upper Triassic Chinle Formation of the Colorado Plateau is a succession of continental deposits that originally extended across much of western North America (3, 4) (Fig. 1). Lithologically similar and strat-

igraphically equivalent rocks of the same age in the Dockum Group of eastern New Mexico and northwestern Texas contain paleocurrents that suggest transport into the Chinle basin, and a connection between the two units has been proposed on that basis (4). We use single-zircon U-Pb data from the basal Dockum Group, together with published data from the Chinle Formation and its correlatives in Nevada (5), to trace a through-going river system between Texas and Nevada in Late Triassic time (Fig. 1).

The Santa Rosa Sandstone is the basal formation of the Upper Triassic Dockum Group, which is widely exposed around the perimeter of the southern High Plains and is in the subsurface of west Texas and eastern New Mexico (6). The Santa Rosa Sandstone rests unconformably on Permian rocks and locally on Middle Triassic rocks [Anton Chico Formation (7)] and is as much as 40 m thick. The sandstone is com-

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monly tabular cross-stratified and parallel laminated and contains beds of chert-pebble conglomerate in laterally extensive, highly quartzose sandstone bodies (8, 9). These features indicate deposition in a sandy braided stream system (10). Santa Rosa fluvial deposits are gradational into

and locally intertongue with deltaic and lacustrine deposits of the overlying Tecovas Formation. Paleocurrent data from the Santa Rosa Sandstone indicate derivation of the alluvium from the region north and east of the present outcrop belt (11). Vertebrate fossils (7) and pollen (12) indicate that the

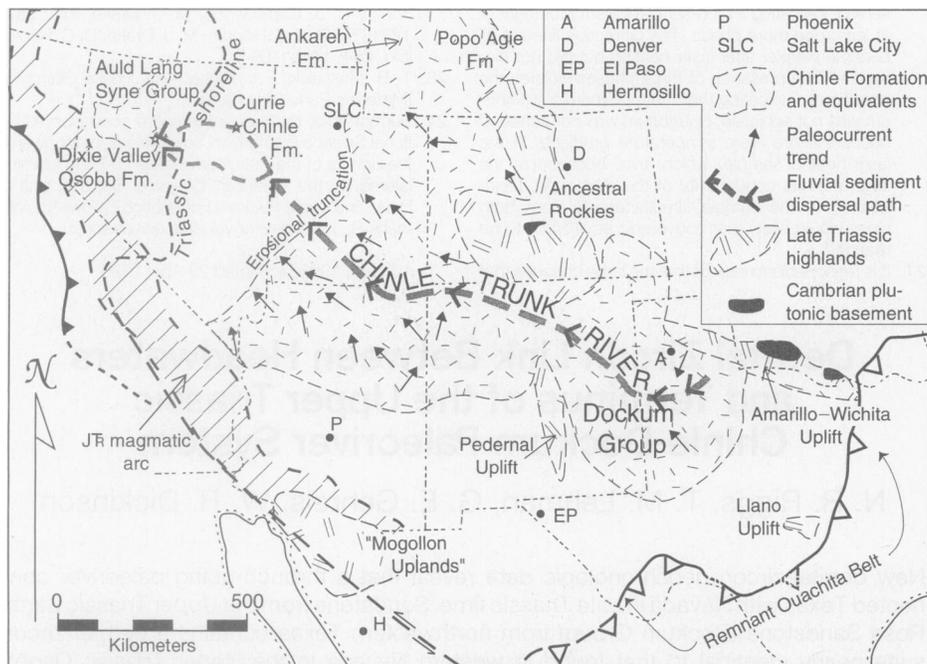
Santa Rosa Sandstone is Late Carnian in age [ $\sim 235$  to 223 million years ago (Ma) (13)]. Biostratigraphic and lithologic similarities suggest that the Santa Rosa is correlative with the Shinarump Member of the Chinle Formation in Arizona, and it seems likely that these strata were contiguous before Paleogene uplift of the central Rocky Mountains and Neogene development of the Rio Grande Rift (14).

We analyzed 17 detrital zircon grains in order to trace the provenance of the Santa Rosa Sandstone (15). These yielded six populations of concordant or near-concordant single-crystal ages (Table 1 and Fig. 2A): 270 Ma ( $n = 1$ ), 390 Ma ( $n = 1$ ), 515 to 525 Ma ( $n = 8$ ),  $\sim 1010$  Ma ( $n = 4$ ), 1425 Ma ( $n = 2$ ), and 2725 Ma ( $n = 1$ ). We enhanced the abundance of the 515- to 525-Ma grains by preferentially selecting distinctive yellow zircons for analysis. Thus, the number of zircons in each population group is not statistically representative.

Zircon ages obtained from the Santa Rosa Sandstone can be readily interpreted as reflecting distinct tectonic sources. The Santa Rosa Sandstone overlies the Permian Quartermaster Formation, which contains  $\sim 270$ -Ma zircon-bearing ash beds (16), along an unconformity with onlapping to the north. Thus, erosion of the Quartermaster ash beds likely supplied zircons to the Santa Rosa Sandstone. Alternatively, although less likely, Permian granites in Chi-huahua and Coahuila, Mexico (17), may have contributed detritus into northward-flowing streams before Late Triassic reworking into the Santa Rosa.

The source of the 390-Ma zircon is less certain. Devonian plutonic rocks are common in the Appalachian orogen and were eroded during the Allegheny orogeny. Slingerland and Furlong (18) suggested that the alluvial wedge shed off the Appalachians may have extended west of the Mississippi Embayment. We thus suggest that Devonian-Carboniferous detritus of Appalachian origin was reworked into the Triassic river system, and that more such material may be present throughout Mesozoic sedimentary strata of the West and Southwest. Other viable sources include (i) Pennsylvanian-Permian sedimentary rocks in Texas that were derived in part from erosion of the Ouachita orogen, which included exposure of Acadian metamorphic (and perhaps plutonic) rocks (19), and (ii) Devonian igneous boulders present in Pennsylvanian flysch-molasse deposits of the Marathon basin (20).

The abundant 515- to 525-Ma grains were clearly derived from Cambrian (21) granitic rocks of the Amarillo-Wichita uplift, as evidenced by paleocurrents in the Santa Rosa Sandstone and by the presence



**Fig. 1.** Late Triassic paleogeographic map showing the proposed location of the Chinle-Dockum trunk river.

**Table 1.** U-Pb isotopic data of the Santa Rosa Sandstone; ppm, parts per million.

Grain type	Concentration (ppm)		Pb isotopic compositions‡			Age (Ma)§		
	U†	Pb	208/206	207/206	204/206	<sup>206</sup> Pb* <sup>238</sup> U	<sup>207</sup> Pb* <sup>235</sup> U	<sup>207</sup> Pb* <sup>206</sup> Pb*
C, An, A	238	11.5	0.22570	0.06636	0.0010138	270 ± 2	269 ± 3	263 ± 19
Ac	126.5	9.4	0.25742	0.07957	0.0017167	391 ± 4	391 ± 6	392 ± 30
C, R	357.7	31.17	0.13883	0.06243	0.0003291	518 ± 2	518 ± 4	516 ± 12
C, R	187.8	16.34	0.12339	0.06492	0.0005095	522 ± 2	520 ± 3	511 ± 12
Y, 2:1	66.1	5.98	0.16204	0.06781	0.0006792	523 ± 5	524 ± 6	527 ± 15
Y, 2:1	90.2	18.15	0.13536	0.06074	0.0002026	519 ± 3	520 ± 3	522 ± 9
Y, 2:1	124.5	11.13	0.16993	0.06479	0.0004954	516 ± 3	516 ± 4	514 ± 11
Y, 2:1	312.9	27.1	0.12188	0.05875	0.0000657	526 ± 3	526 ± 3	522 ± 6
C-Y, 3:1	318.5	28.0	0.14903	0.06065	0.0002065	521 ± 2	520 ± 2	516 ± 6
C-Y, 3:1	105.6	17.2	0.15356	0.22353	0.0114137	522 ± 3	519 ± 12	508 ± 48
C, An, A	217.2	37.0	0.10762	0.07604	0.0002118	993 ± 5	1000 ± 5	1014 ± 5
C, An, A	73.5	13.5	0.15601	0.08042	0.0004925	1016 ± 7	1019 ± 8	1025 ± 8
C, An, A	201.1	36.58	0.15168	0.08759	0.0009627	1000 ± 5	1012 ± 7	1038 ± 10
Pk, R	257.8	45.8	0.13937	0.07753	0.0003281	1005 ± 4	1006 ± 5	1010 ± 6
Pk, R	703.15	166.58	0.01983	0.09021	0.0000174	1429 ± 6	1428 ± 6	1425 ± 4
Pk, R	266.4	69.2	0.14614	0.09328	0.0002409	1400 ± 6	1409 ± 7	1424 ± 5
Pk, R	137.8	91.02	0.31231	0.18926	0.0001059	2657 ± 11	2696 ± 12	2725 ± 4

||C, clear; An, angular; A, abraded; Ac, acicular; R, rounded; Y, yellow; 2:1 and 3:1, length:width; Pk, pink. †U and Pb concentrations have up to 25% uncertainty as a result of uncertainty in the mass of the grain. ‡Isotopic compositions are corrected for blank (5 pg) and 205/235 spike, and for 0.14 ± 0.06% per mass unit fractionation, on the basis of replicate analysis of National Bureau of Standards Pb standards. U composition is corrected for 0.02 ± 0.04% per atomic mass unit fractionation and 1-pg blank. Uncertainties in measured 207/206 = 0.2% to 0.4%, and in measured 204/206 = 0.5% to 5%. §Decay constants used:  $\lambda^{235} = 9.8485 \times 10^{-10}$ ;  $\lambda^{238} = 1.55125 \times 10^{-10}$ ; and  $238/235 = 137.88$ . Data reduction is from Ludwig (30). \*Radiogenic Pb; common lead correction (31) varies with age of zircon.

of Cambrian granite bodies in the subsurface. The Amarillo-Wichita uplift was active during the Pennsylvanian Ouachita orogeny, and possibly during the Late Triassic breakup of Pangaea as well. Late Paleozoic detritus shed to the south and west off the Amarillo-Wichita uplift into depocenters north of the Dockum Basin may also have been reworked into the Dockum section.

Zircons yielding 1010-Ma ages were probably derived from widespread Grenville basement in northern Mexico and the southern and southeastern United States (22). There is little or no indication that Grenville plutonic rocks were exposed in Texas in Triassic time, but zircons could have been reworked from Paleozoic strata derived from the primary sources. Plutons with ages of  $\sim 1400$  Ma are likewise widespread across the south-central United States, and derivative zircons were probably very common in late Paleozoic rocks in the area.

Upper Triassic nonmarine strata of the Chinle Formation in eastern Nevada and correlative marine strata of the Osobb Formation (Auld Lang Syne Group) in central Nevada (Fig. 1) were probably contiguous, based on the observation of a common population of zircons that is distinct from those in any other miogeoclinal and eugeoclinal strata in the western Cordillera (5). This characteristic population includes many zircons with ages of 500 to 525 Ma that are identical in age and morphology to the Cambrian zircons in the Santa Rosa Sandstone of the Dockum Group.

The Chinle Formation near Currie, in eastern Nevada (Fig. 1), contains conglomeratic sandstone and interbedded sandstone and mudstone interpreted as correlative with the Shinarump Conglomerate and Petrified Forest members of the Chinle Formation on the Colorado Plateau (23). The Osobb Formation of central Nevada is a shelf succession that is stratigraphically equivalent to the Chinle Formation (24). Where sampled, it consists of sandstone and argillite and contains some detritus (potassium feldspar and argillite rock fragments) that was probably transported along the continental shelf (5).

The zircon population obtained from the Santa Rosa Sandstone is nearly identical to that from the Osobb Formation of central Nevada (Fig. 2B and Table 1). Basement rocks that contain zircons with ages of 1400 to 1450 Ma are found throughout the southern Cordillera. The same is true for 1000- to 1100-Ma zircons, although this population is not represented in Chinle Formation at Currie. The population with ages of 515 to 525 Ma ties the Nevada Triassic section, including the Chinle For-

mation at Currie, to the Santa Rosa Sandstone. This correlation is further supported by the presence of two younger Paleozoic zircon populations in both formations.

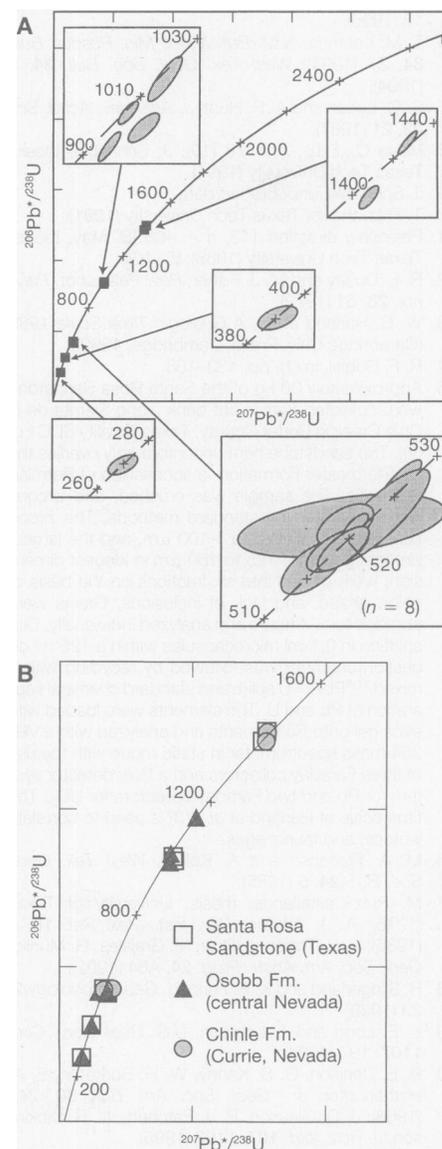
Gehrels and Dickinson (5) proposed that the 265-Ma and 350- to 420-Ma zircons in the Osobb Formation, which are missing from the Currie Chinle Formation, were derived from a Paleozoic Klamath-Sierran oceanic arc to the west. We suggest instead that a through-going river system transported the Devonian and Permian zircons from Texas. Although the percentage of Devonian grains is greater in the Osobb sample (25), their scarcity in the Santa Rosa sample may only reflect a bias in picking.

Basement rocks that range in age from late Proterozoic to Cambrian crop out in Colorado (26) in the area of the Uncompahgre and Front Range uplifts (Fig. 1). Specifically, a syenite suite with U-Pb isotopic age of  $536 \pm 4$  Ma, the Pikes Peak complex at  $1093 \pm 20$  Ma, and abundant volcanic-plutonic complexes with ages of 1440 to 1470 Ma and 1700 to 1740 Ma (26, 27) are similar in age to the zircon populations of the Nevada Chinle and Osobb formations and must be considered as a source area. Other common ages of basement rocks in Colorado (for example, 1350 Ma, 1600 to 1660 Ma, and 1760 to 1770 Ma) are, however, not found in the Nevada or Texas samples. Likewise, potential Devonian and Permian source basement rocks do not occur in Colorado.

The presence of zircons of identical age in the Texas and Nevada samples suggests that a transcontinental river system extended across the southern part of the North American continent. Some zircon grains may have ultimately derived from as far away as the central and eastern United States or in part from eastern Mexico. We infer that the source of the distinctive and abundant Cambrian zircons was the Amarillo-Wichita uplift near the Dockum depocenter, whether as a primary source or reworked from nearby Upper Paleozoic strata. Other, less common Paleozoic zircons were derived from more distant sources and were somewhat randomly incorporated into the river system. The presence of Triassic grains in the Osobb and Currie Chinle samples indicates that mixing of other sources occurred downstream.

Our analysis confirms a previous suggestion that a through-going river system connected Texas with the Cordilleran continental margin across the Colorado Plateau (4) (Fig. 1). Detrital zircon analysis can be used to identify the source of material within fluvial deposits and to determine paths that a river system took between source and terminus.

The Osobb-Lower Chinle-Santa Rosa Sandstone connection indicates that early in Late Triassic time the continental interior was topographically low, although punctuated locally by relict highlands (28). The rising continental arc to the southwest of the Chinle depocenter provided a topographic margin in that direction, but structures related to the breakup of Pangaea had evidently not yet formed. The presence of this river precludes contemporaneous barrier highlands related to the opening Gulf of Mexico or to Cordilleran foreland deformation, although such barriers may have formed later. By late Chinle-Dockum time,



**Fig. 2.** (A) Concordia diagram showing zircon populations in the Santa Rosa Sandstone. Error ellipses are shown at the 95% confidence level. (B) Concordia diagram comparing congruent zircon populations of the Santa Rosa Sandstone (Dockum Group, Texas), Chinle Formation (Currie, Nevada), and Osobb Formation (Auld Lang Syne Group, Dixie Valley, Nevada).

paleocurrents and intraformational unconformities in the rocks suggest that the integrated Chinle-Dockum depositional system was disrupted when rift-related structures began to form (29).

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15. Approximately 30 kg of the Santa Rosa Sandstone were collected from a cut bank along Sierrita de la Cruz Creek in Potter County, Texas [locality SDC1 of (9)]. The sandstone here unconformably overlies the Quartermaster Formation, a succession of Permian red beds. The sample was crushed, and zircons were separated by standard methods. The zircon separate was sieved to  $>100 \mu\text{m}$ , and the largest zircons, generally 125 to 150  $\mu\text{m}$  in longest dimension, were picked into six fractions on the basis of color, shape, and lack of inclusions. Grains were abraded for ~4 hours and analyzed individually. Dissolution in 0.1-ml microcapsules within a 125-ml digestion chamber was followed by recycling with a mixed  $^{205}\text{Pb}$ - $^{235}\text{U}$  spike and standard chemical separation of Pb and U. The elements were loaded with silica gel onto Re filaments and analyzed with a VG-354 mass spectrometer in static mode with the use of three Faraday collectors and a Daly detector system for Pb and two Faraday collectors for  $\text{UO}_2$ . The time scale of Harland *et al.* (13) is used to correlate isotopic and faunal ages.
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# Late Proterozoic and Paleozoic Tides, Retreat of the Moon, and Rotation of the Earth

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The tidal rhythmites in the Proterozoic Big Cottonwood Formation (Utah, United States), the Neoproterozoic Elatina Formation of the Flinders Range (southern Australia), and the Lower Pennsylvanian Pottsville Formation (Alabama, United States) and Mansfield Formation (Indiana, United States) indicate that the rate of retreat of the lunar orbit is  $d\xi/dt \sim k_2 \sin(2\delta)$  (where  $\xi$  is the Earth-moon radius vector,  $k_2$  is the tidal Love number, and  $\delta$  is the tidal lag angle) and that this rate has been approximately constant since the late Precambrian. When the contribution to tidal friction from the sun is taken into account, these data imply that the length of the terrestrial day 900 million years ago was ~18 hours.

The well-known tides induced on Earth by the sun and moon have had several long-term effects over the age of Earth. Most notably, the transfer of angular momentum from Earth to the moon has resulted in an appreciable increase in the length of the day and a retreat of the moon from Earth. Here, we used laminated tidal sediments to determine tidal periods back to 900 million years ago. From these records, the retreat rate of the moon—that is, the evolution in time of the lunar semimajor axis—can be calculated. In principle, the information derived from tidal rhythmites (tidalites) can also yield the rotational deceleration of Earth, the change in the length of day (LOD), the rate of generation of terrestrial tidal frictional heat, and the variation with time of the product of  $k_2$  and  $\sin(2\delta)$ . Tid-

alites consist of stacked sets (commonly of millimeter to centimeter scale) of laminated mudstone or intercalated beds of sandstone and mudstone; successive sets exhibit progressive vertical thickening and thinning in response to daily changes in current velocities associated with tidal processes. Tidalites from a variety of modern settings—including delta fronts, abandoned tidal channels, tidal flats, and estuaries—have been described (1).

The most common reported tidal cyclicities in the rock record include daily, semidaily, and semimonthly periods. Semimonthly (neap-spring) periods reflect phase changes of the moon during the half-synodic month and lunar declinational changes associated with the half-tropical month (2). During the synodic month, tides are higher when Earth, the moon, and the sun are nearly aligned (syzygy) and are lower when the radius vectors from Earth to the sun and moon enclose a right angle (quadrature). Spring tides form during syzygy (full and new moon), whereas neap tides form during quadrature (the waxing and waning phases of the moon) (3). Deviations from tidal equilibrium are always encountered in the tidal record (4); these deviations result from local tidal geometry and variable basinal

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