Stratigraphic investigations of carbon isotope anomalies and Neoproterozoic ice ages in Death Valley, California

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ABSTRACT

An unusual richness of biogeochemical events is recorded in Neoproterozoic–Cambrian strata of the Death Valley region, California, United States. Eight negative carbon isotope (δ13C) excursions are found in carbonate units between 1.08 Ga and the Precambrian/Cambrian boundary; four of these excursions occur in carbonates that contain textural features similar to those found globally in postglacial “cap carbonates” (including one or more of the following: laminite with rollup structures, apparent “tube rocks,” seafloor precipitates, and sheet-crack cements). However, only two of these units, the Sourdough limestone member of the Kingston Peak Formation and the Noonday Dolomite, rest directly upon glacial strata. The basal Beck Spring Dolomite and the Rainstorm Member of the Johnnie Formation each contain negative excursions and cap-carbonate–like lithofacies, but do not rest on known glacial deposits. If the negative δ13C excursions are assumed to record depositional processes, two equally interesting hypotheses are possible: (1) The Death Valley succession records four glacial pulses in Neoproterozoic time, but glacial units are not preserved at two stratigraphic levels. (2) Alternatively, other global oceanographic processes can cause negative excursions and cap-carbonate–like facies in addition to, or independent of, glaciation.

Keywords: chemostratigraphy, Death Valley, Earth history, glaciation, Neoproterozoic, stratigraphy, carbon isotopes.

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INTRODUCTION

The dawn of the Phanerozoic is one of the most fascinating times in the development of the biosphere (Cloud, 1988; Knoll and Walter, 1992; Lipps and Signor, 1992). With the advent of new analytical techniques (isotopic and molecular, for example), incredible fossil discoveries (e.g., metazoan embryos, Xiao et al., 1998), and a broadened interest in early animal evolution, the Neoproterozoic has become a focal point for integrated geobiological studies. The Neoproterozoic is characterized by climate extremes that may be unrivaled in the Phanerozoic (e.g., snowball Earth) (Kirschvink, 1992; Hoffman et al., 1998b). Speculations with regard to the effects of this severe climatic deterioration on life (recorded in the geologic record as low-latitude glacial diamictites, extreme perturbations in the biogeochemical cycles of carbon and sulfur, and unusually textured carbonate seafloor cements) have been proposed (Harland and Rudwick, 1964; Kirschvink, 1992; Kaufman et al., 1997b; Hoffman et al., 1998b; Knoll and Carroll, 1999). These speculations are based, however, on chronostratigraphic frameworks that are limited in biostratigraphic resolution and radiometric age constraints, as well as omissions in stratigraphic records characteristic of continental-margin successions.

In carbonate-dominated strata, temporal variations in carbon, sulfur, and strontium isotope compositions of well-preserved samples hold great promise for regional correlation. Global correlation is more problematic insofar as siliciclastic strata dominate many key successions, thus impeding the construction of continuous isotope trends regardless of the degree of preservation. The large number of publications purporting a composite “Neoproterozoic reference section” is testament to the general acceptance of isotope stratigraphy as a critical tool in this ancient interval. Unfortunately, it is also a manifestation of the ambiguity inherent in constructing global paradigms from local systems. This is the “pre-Cambrian correlation problem” in sum: the absence of rigorous biostratigraphic control or high-resolution radiometric age dates, the eccentricities of each sedimentary basin may be given global significance with few independent tests to evaluate the purported significance. Excellent preservation (e.g., lack of metamorphism, structural simplicity, and good exposure) is not a guarantee of stratigraphic completeness. Thus, researchers working on variably segmented and preserved stratigraphic successions around the world disagree on something as basic as the number of glaciations in Neoproterozoic time (e.g., Kaufman et al., 1997b; Hoffman et al., 1998b; Saylor et al., 1998; Kennedy et al., 1998; Crowell, 1999; Knoll, 2000; Brasier et al., 2000; Walter et al., 2000).

The Death Valley area of eastern California/western Nevada, United States, contains a thick, intensely studied stratigraphic package spanning from late Mesoproterozoic through middle Paleozoic time (Cloud, 1973). The area is well known for its structural complexity and long tectonic history; the succession is replete with stratigraphic breaks of unknown duration. Few radiometric dates are available and, except for stromatolites and rare microfossils, the Proterozoic sedimentary rocks are poorly fossiliferous. Accepting these caveats, Death Valley strata nonetheless provide an opportunity to study the extreme climatic perturbations recorded in Neoproterozoic time. The regional sequence stratigraphy is well documented, and the physical succession of strata is relatively unambiguous. If one works around the moderately intricate structural re-
lationships in the area, it is possible to walk though the entire package, from late Mesoproterozoic through Ordovician strata (see volumes edited by Cooper et al. [1982] and Cooper and Stevens [1991]). Notably, glacial diamictons (Miller, 1982, 1983, 1985, 1987; Prave, 1999) are found at several stratigraphic horizons and are overlain by texturally and isotopically unique “cap carbonates” (Corsetti, 1998; Prave, 1999; Corsetti and Hagadorn, 2000; Corsetti et al., 2000). In this paper, we present a basin-scale integrated stratigraphy, supported by high-resolution isotopic analysis of thick carbonates in multiple equivalent sections along and across the ancient depositional system. It is important to note, however, that in certain portions the succession is predominantly siliciclastic. The isotopic records are therefore discontinuous through some stratigraphic intervals. Although the clear trends defined by closely spaced samples are testament to the excellent preservation of depositional carbon isotope (δ13C) variations, sample alteration is addressed by the use of petrographic, cathodoluminescent, and/or geochemical screens (see Kaufman and Knoll [1995] for a discussion of the methods). The relative sequence of environmental and climatic events preserved in Death Valley will be used to test predictions from other Neoproterozoic basins worldwide.

Geologic Background

The Death Valley section consists of (in ascending order) the Pahrump Group (the Crystal Spring Formation and Beck Spring Dolomite, and the Kingston Peak Formation), the Noonday Dolomite, the Johnnie Formation, the Stirling Quartzite, and the Wood Canyon Formation (which contains the Precambrian/Cambrian boundary) (Stewart, 1966, 1970; Wright et al., 1974a; Corsetti and Hagadorn, 2000) (figs. 1A, 1B). The Death Valley section is locally >6 km thick, but averages ~4.5 km (Stewart, 1966, 1970; Wright et al., 1974a).

Crystal Spring Formation

The Crystal Spring Formation, the basal member of the Pahrump Group, is a mixed siliciclastic-carbonate succession that ranges in thickness from ~450 to 1200 m (Roberts, 1982). The Crystal Spring rests on 1.7 Ga metamorphic basement intruded by 1.4 Ga granitoid rocks (Labotka, 1978). Diabase sills dated at ca. 1.087 Ga intruded the lower part of the formation (Heaman and Grotzinger, 1992). In some areas, the intrusions reacted with the carbonate rocks and formed the distinctive talc deposits that are apparent around the Death Valley area (Wright and Troxel, 1965). An angular unconformity has been recognized within the formation above the diabase (Mbuyi and Prave, 1992, 1993). Carbonates below and above this intrusion contain stromatolites of limited biostratigraphic utility (Awramik et al., 2000). Our study focuses on the “upper units” (Wright et al., 1974a; Roberts, 1982), consisting of a coarsening-upward sequence of shale-siltstone-quartzite with minor carbonate near the base and at the top (~150 m).

Beck Spring Dolomite

The basal Beck Spring Dolomite records a flooding event, as the underlying coarse-grained siliciclastic and carbonate rocks of the upper Crystal Spring Formation are overlain by very finely laminated carbonates of the Beck Spring Dolomite; some have considered this contact conformable (Marian, 1979), whereas others have considered it a discontinuous sequence boundary (Mbuyi and Prave, 1992, 1993). The lower 200 m contains finely laminated dolostone that displays abundant soft-sediment deformation, rollup structures (Fig. 2A), breccias, and some megabrecias, interpreted as slope deposits. The middle 100 m contains oolitic packstones, grainstones, and stromatolites, and the remaining Beck Spring Dolomite contains mostly cherty grainstone with some stromatolites. The oolitic units commonly contain “giant ooids” characteristic of late Precambrian time (Fig. 2B). The formation represents typical shoaling and progradational carbonate-platform sedimentation; deeper-water sedimentation is recorded in the lower part, and shallow subtidal to peritidal parasequence sets constitute the upper part. A deep karst surface is present at the top of the main body of the Beck Spring Dolomite, and several beds of thin carbonates in shale are present between the main body of the Beck Spring Dolomite and the overlying siliciclastic-dominated Kingston Peak Formation. We follow recent convention and denote these the “transition beds” (e.g., Link et al., 1993). However, the karst may suggest a more significant break at this stratigraphic position; thus, the transition beds may not be depositionaly intermediate.

The age of the Beck Spring Dolomite is unknown, but certainly postdates 1.08 Ga. The vase-shaped microfossil Melanocyrillium (Horodyski, 1987) is found in the transition beds. It is not known whether Melanocyrillium or other vase-shaped microfossils have correlative potential; similar taxa do occur in the Chuar Group in the Grand Canyon area beneath an ash dated at 742 ± 6 Ma (Porter and Knoll, 2000; Karlstrom et al., 2000; DeRivry et al., 2001). If this regional correlation holds, it would constrain the Beck Spring Dolomite to be older than ca. 742 Ma (but younger than 1.08 Ga). However, vase-shaped microfossils have been interpreted to represent testate amoebae (Porter and Knoll, 2000), an extant group, and thus the correlation is tenuous.

Kingston Peak Formation

The Kingston Peak Formation is a heterolithic unit containing turbidites, shallow-marine and possibly fluvial sandstones, siltstones, conglomerate, dropstones (Fig. 2C), diamicite, ironstone, organic-carbon–rich laminated carbonates, and volcanic rocks (Troxel, 1982b; Miller, 1982, 1983, 1985). Facies change rapidly across the basin, indicating deposition in an actively extending tectonic environment (Wright and Troxel, 1966; Miller, 1985). The correlations proposed by Prave (1999) and the informal terminology proposed by Miller (1982) form the framework within which we interpret the Kingston Peak Formation as a whole to contain two glacially derived intervals each overlain by carbonates. The lower diamictites of the Surprise member (including an iron-rich dropstone-laden mudstone facies) are overlain by the finely laminated Sourdough limestone member. The upper-basement and quartzite-clast diamictites of the Wildrose member are overlain by the Noonday Dolomite. At Goler Wash, we have observed an iron-rich dropstone-laden facies above the basement-clast diamictite immediately beneath the Noonday Dolomite contact, as well. Other thin carbonates are known from the Kingston Peak Formation: A thin, microfossiliferous, wavy-laminated and oncoid-bearing unit is known from within or capping the lower diamictites in the Kingston Range (Pierce and Cloud, 1979; Troxel et al., 1987; Awramik et al., 2000). We interpret this unit as a probable onshore equivalent to the Sourdough limestone member. An unnamed limestone unit located stratigraphically above the Sourdough limestone member and below the Noonday Dolomite in the Panamint Range area contains shallow-water carbonate lithofacies, including oncoids. Other workers may have mistaken this unit for the Noonday Dolomite (see Prave, 1999).

Despite the presence of a moderately diverse microfossil assemblage of nondiagnostic Proterozoic age (Pierce and Awramik, 1994), no independent age constraints are currently available for the Kingston Peak Formation. However, the presence of diamicrite, volcanic rocks, ironstone, and evidence for syndeposi-
tional normal faulting (e.g., Miller, 1985) led some workers to correlate the Kingston Peak Formation with the rift-related Rapitan Group in northwest Canada (ca. 750 Ma) (Stewart and Poole, 1974; Stewart and Suczek, 1977). Prave (1999) suggested that the lower part of the formation may correlate to these units, but that the upper part may be much younger (ca. 600 Ma) (Walker et al., 1986). This interpretation would imply that >100 m.y. of time would be represented by the relatively thin stratigraphic package between the Sourdough limestone member and the Noonday Dolomite (an alternative view is presented subsequently herein). The relationship between the Kingston Peak Formation and overlying strata is complex: An angular unconformity is present in many areas (Wright and Troxel, 1966; Christie-Blick and Levy, 1989), whereas the contact appears genuinely conformable in other areas (Prave, 1999; Corsetti et al., 2000).

Noonday Dolomite
The Noonday Dolomite exhibits a myriad of unusual carbonate textures that are common in carbonates that cap Neoproterozoic glacial diamictites worldwide. At the base, ubiquitous isopachous cements line horizontal sheet cracks and “pseudostromatolites” vugs (Fig. 3). The lower part of the formation has been interpreted to contain large domes (up to ~200 m in diameter) interpreted as megastromatolites (Wright et al., 1974b, 1978; Cloud et al., 1974; Williams et al., 1974a, 1974b) that approach the shelf margin; basinal facies are found to the west in the equivalent Ibex Formation and include megabreccias, carbonate turbidites, and laminites (Troxel, 1982a). Tubular (or apparently tubular) structures of probable biologic affinity (Marenco et al., 2001), several centimeters in diameter and up to 100 cm in length, are found to be subvertical within the domes (Cloud et al., 1974; Wright et al., 1978) and in other areas without purported domal builds (Corsetti et al., 2000) (Fig. 3). These same structures have since been interpreted to represent gas escape structures from methane cold seeps (Kennedy et al., 2001b). In addition, crystal “bushes” are also recognized on the extreme flanks of the domes from the middle part of the lower Noonday Dolomite. They are poorly pre-
served, and their affinity is not known, but the external morphology is not unlike a calcareous algae (cf. Epiphyton) rather than abiotic crystal fans. Sandy dolomite dominates the upper part of the Noonday Dolomite at most localities (Stewart, 1970). The lower and upper parts of the Noonday Dolomite are separated by a notable sequence boundary with at least tens of meters of local relief (Summa et al., 1991, 1993a, 1993b; Summa, 1993) and possibly as much as 100 m of relief. The contact between the Noonday Dolomite and the overlying Johnnie Formation has been considered conformable (Stewart, 1970; Benmore, 1978; Christie-Blick and Levy, 1989). However, Summa (1993) demonstrated the presence of karst at the top of the Noonday and hypothesized a significant stratigraphic break of unknown duration.

The age of the Noonday Dolomite is uncertain, although Wright et al. (1978) suggested that the presence of Dzhelindia (a clotted structure interpreted as a possible calcimicrobe) was consistent with a Riphean age (ca. 900–700 Ma). Previous chemostratigraphic studies have alternately correlated the Noonday Dolomite with Sturtian (ca. 700 Ma; Corsetti, 1998; Corsetti et al., 2000) and Varangian deposits (ca. 600 Ma; Prave, 1999), respectively.

Johnnie Formation
The Johnnie Formation contains mixed siliciclastic-carbonate lithofacies interpreted to represent shallow-marine deposition with minor fluvial influence (Stewart, 1970; Benmore, 1978; Summa et al., 1991, 1993a, 1993b; Summa, 1993). Stromatolites are abundant in the carbonate units (Benmore, 1978). Several regionally persistent shallowing-upward sequences truncated by fluvial quartzites and/or karstic carbonates are present within the Johnnie Formation, separated by paraconformities of unknown temporal magnitude (Summa, 1993). A regionally extensive marker bed, the Johnnie oolite, occurs in the upper part of the formation (Rainstorm Member, e.g., Stewart, 1966, 1970) (Fig. 4). Summa (1993) and Summa et al. (1994) suggested the presence of a major sequence boundary at the base of the laterally persistent oolite marker bed. Although no incised valleys are known from this stratigraphic level, the clear juxtaposition of deeper-water facies (below storm wave base) beneath the shallow-water, cross-bedded oolite suggests a depositional hiatus. On the craton, karst has been recognized at the base of the oolite (C. Fedo, 2001, personal

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**Figure 1.** (Continued.)

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**Figure 2.** (A) Rollup structures from the basal Beck Spring Dolomite, Alexander Hills section (see location in Fig. 6). (B) Giant ooids characteristic of the Beck Spring Dolomite. These occur as clasts in the overlying Kingston Peak Formation and the Rainstorm Member of the Johnnie Formation. (C) Large dropstone of Beck Spring Dolomite within the iron-rich turbidites of the Kingston Peak Formation, Sperry Wash, eastern Death Valley.
The post-oolite Rainstorm Member contains a sequence of interference-ripple cross-laminated quartzite, siltstone, and shale with local preservation of thick carbonates. The carbonates are distinctively pink, continue for >50 m in some exposures, and contain intraclastic or peloidal grainstones punctuated by beds characterized by calcite pseudomorphs of small aragonite crystal fans that apparently grew on the ancient seafloor (Fig. 4).

In addition to several smaller-magnitude sequence boundaries, a major incision surface cuts into the upper part of the Johnnie Formation (Summa et al., 1991, 1993a, 1993b, 1994; Summa, 1993) (Fig. 4). The surface removes the Johnnie oolite at certain localities along section (implying up to 150 m of erosional relief) (Summa, 1993; Levy et al., 1994; Charlton et al., 1997). Incised-valley fill consists of subangular blocks of varied lithology in a sandstone or mudstone matrix and
includes large clasts of the Johnnie oolite, lower Johnnie Formation stromatolites, and Beck Spring Dolomite (Fig. 4). It is notable that readily identifiable clasts of lower Johnnie and Beck Spring lithotypes are found within the incised-valley fill in the Nopah Range, potentially indicating several kilometers of regional uplift and erosion during or near upper Johnnie time (cf. Summa, 1993) (see subsequent discussion). The remaining Johnnie Formation consists of featureless dark green mudstones (Moore, 1974; Charlton et al., 1997) that become progressively sandy up section to the contact with the overlying Stirling Quartzite. A finely laminated micritic limestone is also found within this interval.

The occurrence of the stromatolite Boxonia has, however, not been confirmed, as it is found as clasts in the incised-valley fill. Christie-Blick and Levy (1989) and Abolins et al. (2000) tentatively correlated the large incision to sea-level drawdown associated with “Marinoan” age glaciation on the basis of sequence stratigraphic correlation with units in Utah (see discussion in Corsetti et al., 2000), rather than regional uplift (e.g., Summa, 1993). If correct, preincision beds are likely to be older than 580 Ma, the age of postincision volcanic rocks of the Brown’s Hole Formation, Utah (Christie-Blick and Levy, 1989). Unfortunately, there is no independent chronostratigraphic evidence to support this correlation.

Stirling Quartzite
The Stirling Quartzite is predominantly composed of coarse-grained siliciclastic rocks, with minor carbonate layers, interpreted to represent continental braiblaid to marginal-marine paleoenvironments (Fedo and Cooper, 2001). Carbonates are noted in the middle of the Stirling in possibly lagoon-like facies and in the D member (of Stewart, 1966, 1970) found in more offshore localities. Problematic calcareous fossils have been reported from the D (Langille, 1974) and C members and have been related to Cloudina (cf. Hagadorn et al., 2000), suggesting a “latest Proterozoic” age. The available data would suggest an age younger than 580 Ma but older than 544 Ma (the Precambrian/Cambrian boundary, see next section) (Corsetti and Hagadorn, 2000).

Wood Canyon Formation
The Wood Canyon Formation is formally subdivided into the predominantly marine Lower Member, the conglomeratic, continental braiblaid-dominated Middle Member, and the mixed siliciclastic-carbonate marine Upper Member (Stewart, 1966, 1970; Diehl, 1979; Fedo and Cooper, 1990, 2001; Fedo and Prave, 1991). The Lower Wood Canyon Formation, of primary interest here, can be divided into three siliciclastic-carbonate shoaling-upward parasequences (Prave et al., 1991; Corsetti and Kaufman, 1994; Horodyski et al., 1994; Corsetti and Hagadorn, 2000). Ediacaran fossils, including Ernietta (Horodyski, 1991) and Swartpuntia (Hagadorn and Waggner, 2000), have been reported from the siliciclastic beds above the contact between the Stirling Quartzite and Lower Wood Canyon Formation. Trepตืกขนนหู pedum, the fossil used to correlate the Precambrian/Cambrian boundary, occurs several tens of meters above the Ediacaran fossils in the siltstones of the third parasequence, between the second and third carbonate units (Horodyski et al., 1994; Runnegar et al., 1995; Hagadorn, 1998; Hagadorn and Waggner, 1998; Corsetti and Hagadorn, 2000). A mildly diverse Early Cambrian fauna—including olenellid trilobites, archaeocyaths, hyoliths, and inarticulate brachiopods—are known from the Upper Wood Canyon Formation (Stewart, 1970; Fritz, 1975, 1993; Mount et al., 1991).

Tectonic Setting
In the most general sense, pretrilobite strata in the southern Great Basin are thought to have been deposited in response to the Neoproterozoic rifting of western North America and the formation of a passive margin (Stewart, 1970; Stewart and Poole, 1974; Stewart and Suczek, 1977; Bond, 1997) (Fig. 5). Geo-logic evidence for rifting is found in the Kingston Peak Formation, including volcanic units deposited in extensional basins, tentatively correlated to other well-known rift-related sequences in North America (e.g., the ca. 750 Ma Rapitan Group in northwestern Canada) (Stewart and Poole, 1974; Miller, 1987; Fedo and Cooper, 2001). Thermal-subsidence modeling, however, would predict a much younger age for the onset of thermal subsidence, between 625 and 540 Ma (Armin and Mayer, 1983; Bond et al., 1985; Levy and Christie-Blick, 1991; Bond, 1997). This potentially long offset in rift age vs. the onset of thermal subsidence, coupled to the lack of radiometric constraints, has spawned a host of possible tectonic interpretations (Stewart and Poole, 1974; Levy and Christie-Blick, 1991; Prave, 1999; Corsetti et al., 2000; Fedo and Cooper, 2001). At this point, the controversy will only be resolved with improved age constraints.

The tectonic setting of the pre-Kingston Peak units (the Crystal Spring Formation and the Beck Spring Dolomite) is more poorly understood. It is likely that the Crystal Spring Formation and Beck Spring Dolomite were part of an extensive cratonal cover sequence and were preserved in grabens as a result of
block faulting during extension and deposition of the Kingston Peak strata (Stewart, 1970; Heaman and Grotzinger, 1992). Previous workers considered the Pahrump Group to have been deposited in an “aulacogen” on the basis of presumed facies patterns and a trough-like paleogeography (e.g., Wright et al., 1974a). However, palinspastic reconstruction of the region (e.g., Levy and Christie-Blick, 1989) demonstrated that the trough shape of the basin may be due to later tectonic juxtaposition. In addition, Heaman and Grotzinger (1992) argued that the so-called aulacogen was simply too long lived (from pre-1080 Ma to as young as 600 Ma) to be geologically reasonable. Recognition of an intra–Crystal Spring Formation unconformity (Mbuyi and Prave, 1993) and the deep karst at the top of the Beck Spring Dolomite highlight the discontinuous nature of Pahrump Group sedimentary preservation. Further work is required to decipher the detailed tectonic history of the pre–Kingston Peak units.

CHEMOSTRATIGRAPHY OF THE DEATH VALLEY SUCCESSION

Several key sections from the Death Valley area were chosen for geochemical analysis on the basis of their structural simplicity and completeness, as well as supporting sequence and biostratigraphic data (Fig. 6; Table 1). The entire succession can be traversed at the combined southern Nopah Range sections (Nopah Range 1 and Nopah Range 2) plus Alexander Hills section as well as at the Kingston Range section. A high-resolution chemostatigraphic profile was generated for the Beck Spring Dolomite at the Alexander Hills section. The isotopic data are available.1

Where noted, we have combined our data with that of Corsetti and Kaufman (1994), Prave (1999), and Corsetti and Hagadorn (2000). Other geochemical data are available for different parts of the succession (Tucker, 1986; Zempolich, 1989; Strauss and Moore, 1992; Kenny and Knauth, 1992, 2001). However, few of the papers covering these other data contain the detailed stratigraphic information needed to plot the samples with temporal meaning. Thus, these data are acknowledged but not included here, although they broadly fit the trends outlined herein.

SAMPLE PRESERVATION

Samples from the Great Basin sections were treated in the manner outlined in Kaufman and Knoll (1995) to evaluate postdepositional alteration; this approach included analysis of the petrographic fabrics and cathodoluminescence prior to microdrilling (to avoid the ambiguities inherent in whole-rock analysis) of nonluminescent micrites, microspar, and ooids from polished sections. Elemental and oxygen isotope analyses have regularly been used to evaluate degrees of meteoric alteration of Phanerozoic marine carbonates (Veizer, 1983a, 1983b; Popp et al., 1986) and later adopted for Neoproterozoic samples (Kaufman et al., 1991). However, given that strong environmental gradients (i.e., anoxic oceans, extreme cold, and extensive sea ice) characterized Neoproterozoic glacial cycles, the enrichment of Mn (and Fe) and strong depletion of 18 O in some cap-carbonate lithofacies may faithfully be recording primary seawater compositions. In general, the geochemical analyses should be used as guidelines, recognizing that unique primary events might otherwise be interpreted as diageneric variants.

A number of samples were processed for coexisting organic carbon as well as carbonate carbon isotopes (see footnote 1). The generally constant fractionation (Knoll et al., 1986; Hayes et al., 1999) between carbonate and or-

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1 GSA Data Repository item 2003105, stratigraphic and isotopic data from carbonates in Neoproterozoic to Cambrian strata of Death Valley, California, USA, is available on the Web at http://www.geosociety.org/pubs/tfb2003.htm. Requests may also be sent to editing@geosociety.org.
ganic carbon pairs provides an additional level of confidence that primary seawater variations are preserved. However, in the organic-carbon-rich carbonates at the base of the Beck Spring Dolomite and in the Sourdough limestone member cap carbonate, as well as in organic-carbon-poor crystal-fan beds of the Rainstorm Member of the Johnnie Formation, carbon isotope fractionation is strongly attenuated; the δ13C values of organic carbon are increased by up to 15‰ relative to beds above and below. The 13C enrichment is presumed to reflect nearly original depositional conditions, as no evidence for postdepositional alteration of these particular stratigraphic intervals is present.

Much of the section contains dolomite and thus does not reliably retain the strontium isotope composition of ancient seawater. Thus, the 87Sr/86Sr was not routinely processed for the Death Valley succession. Given the smooth δ13C trends defined by our high-resolution sampling of petrographically screened carbonates, it is most likely that near-primary δ13C variations are preserved, although environmental variance of a few per mil across the depositional basin is expected (Kauffman et al., 1991) and stratal omissions at unconformities complicate the construction of composite curves in any basin (Kauffman et al., 2000). A comparison of geologic and isotopic features characteristic of each formation is provided (Fig. 7).

Integrated Stratigraphy

Crystal Spring Formation

Compared to all other formations in the Death Valley succession, the least is known of the basin architecture and chemical stratigraphy of the silicilastic-dominated Crystal Spring Formation. The 1‰ variability in δ13C compositions (ranging between −5.1‰ and +5.1‰) of the intercalated thin carbonate beds (Alexander Hills, Kingston Range, Saratoga Springs area sections) may be a function of several factors, including primary temporal changes, diagenetic or metamorphic resetting, hiatus, or environmental variance (cf. Kaufman et al., 2000). The intrusion of the Mesoproterozoic diabase, low sample density, and likelihood of sub−Beck Spring erosion makes interpretation of temporal variations in this unit, which requires greater study, problematic.

Beck Spring Formation

The Beck Spring Dolomite was sampled at the Kingston Range, Saratoga Springs area, and Alexander Hills sections (Fig. 8). Three additional sections of the basal Beck Spring Dolomite were collected along strike at the Alexander Hills section to confirm lateral continuity of the isotopic signatures, and organic-carbon isotopes were processed for the Kingston Range and Saratoga Springs area sections to confirm the veracity of the carbonate δ13C record. Except in rare cases, there is good agreement between the carbonate-carbon and organic-carbon pairs. The section at Saratoga Springs area is notable in that it contains some limestone, whereas the other sections are entirely dolostone. In addition, the form of the isotopic curve for the Saratoga Springs area mimics that of the other sections studied, but is offset ~2‰ more negative. For all sections, carbonate isotope values are negative or near zero in the initial 10 m and rise to as high as +5.8‰ within the ~100-m-thick basin Beck Spring Dolomite interval of deeper-water limestones, breccia breccia of laminitae, rollup structures, and resemented carbonates. The greater variance in δ13C in this interval (relative to upper Beck Spring Dolomite beds) may be due to sedimentary mixing, because many of the beds contain transported material. The δ13C values remain similar through the next interval (~50 m), which is dominated by shallow-water deposits capped by giant ooids. Above this horizon, δ13C values shift to ~+3‰ and remain consistently positive for ~100 m through a series of meter-scale subtidal to peritidal shallowing-upward cycles. Toward the top of this cycle stack, δ13C values again shift in a positive direction to ~+4‰ (at the Alexander Hills section, a prominent exposure surface marks the jump to values indicating 13C enrichment). At all localities, the uppermost Beck Spring Dolomite is marked by a negative excursion recorded in both carbonate carbon and coexisting organic carbon. At the Kingston Range section, this excursion occurs over 100 m (and reaches a nadir of ~6‰); at the Saratoga Springs area section, the event is telescoped down to 50 m (and reaches as low as ~4‰); and at the Alexander Hills section, the excursion is recorded in a mere 20 m (and reaches ~1‰). The latter two sections appear truncated by sub−Kingston Peak erosion. The data presented in Prave (1999) from the Alexander Hills are a close match to our high-resolution analyses presented from the same range.

Kingston Peak Formation

The Kingston Peak Formation is predominantly silicilastic; no regionally persistent carbonates are currently known from the formation although locally developed carbonate facies are recognized (Fig. 9). The thin, basal Kingston Peak Formation carbonates—interbedded with mudstones within the first 20 m above the contact with the Beck Spring Dolomite in the Kingston Range and Alexander Hills sections—record predominantly positive δ13C values. Those recorded at the Kingston Range section are between +2.0‰ and +3.1‰ (Fig. 8), i.e., slightly more positive than the Alexander Hills samples, and co-occur with vaso-shaped and other microfossils (Horodyski and Mankiewicz, 1990). At the Kingston Range locality, a thin, locally persistent fossiliferous and oncocid-rich carbonate (Pierce et al., 1977; Pierce and Cloud, 1979; Awramik et al., 2000) is found ~200 m above the transition beds; this carbonate possibly caps the lower diaminites. From the base to the top, this unit records a strong positive δ13C trend from ~4.1 to +1.1‰. In the Panamint Range to the west, the organic-carbon-rich, finely laminated Sourdough limestone member caps the lower Kingston Peak Formation diaminite succession and records δ13C values from −2.4‰ to −1.6‰ in Goler Wash and −3.1‰ and −2.9‰ in Pleasant Canyon. Prave (1999) presented additional data from Redlands Canyon in the same region that demonstrates a continuation of the isotopic trend to values as high as +2‰ (strikingly similar to the oncoid layer in Kingston Range). In the northern part of the Panamint Range at Tucki Mountain, the shallow-water carbonates of the unnamed limestone record δ13C values between +4.7‰ and +5.3‰, confirming the data presented by Prave (1999).

Noonday Dolomite

The Noonday Dolomite was sampled in the Nopah Range I and Winters Pass Hills sections (Fig. 9). The microbially laminated lower Noonday Dolomite records consistently negative δ13C values (~−3‰) in association with sheet-cratck cement fabrics, crystal “bushes,” and enigmatic tubes (Cloud et al., 1974). A 1‰–2‰ positive step in values is noted across a significant sequence boundary (as recognized by Summa, 1993) in sandy dolostones of the upper Noonday Dolomite.

Johnnie Formation

The Johnnie Formation was sampled in the Nopah Range, Winters Pass Hills, and Alexander Hills sections, and our chemostratigraphic framework has been integrated with the detailed sequence stratigraphic analysis provided by Summa (1993) (Fig. 10). The Winters Pass Hills section is thinner than the two Nopah Range sections and represents a more “cratonic” expression of the Johnnie Formation. Two sections were measured in the
<table>
<thead>
<tr>
<th>Stratigraphic position of negative isotopic anomaly</th>
<th>Location sampled</th>
<th>Magnitude of excursions</th>
<th>Stratigraphic duration of negative excursion</th>
<th>Shape of negative anomaly</th>
<th>Presence of known underlying diamictite</th>
<th>Iron enrichment in underlying unit</th>
<th>Organic rich</th>
<th>Sequence architecture</th>
<th>Lowest δ¹³C</th>
<th>Overall diagnosis</th>
<th>Carbonate textures</th>
<th>Other notable features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basal Beck Spring Dolomite</td>
<td>Alexander Hills (AH), Kingston Range (KR), Saratoga Springs (SSP)</td>
<td>6 %e</td>
<td>10 m</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>flooding surface</td>
<td>fabric retentive dol. (some is at S3p)</td>
<td>organic rich laminites, small and large rollup structures</td>
<td>chip breccia of laminites indicating basinal setting</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uppermost Beck Spring Dolomite</td>
<td>Alexander Hills (AH), Kingston Range (KR), Saratoga Springs (SSP)</td>
<td>6 %e</td>
<td>up to 100 m</td>
<td>no</td>
<td>no</td>
<td>yes</td>
<td>highstand</td>
<td>normal to slightly reduced</td>
<td>karst, variable silification</td>
<td>none</td>
<td>top beds contain Melanocyrtium and sheet-like calcareous algae</td>
<td></td>
</tr>
<tr>
<td>Kingston Peak oncolite bed</td>
<td>Kingston Range (KR)</td>
<td>3 %e</td>
<td>3 m</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>normal</td>
<td>fabric retentive dol. minor silification</td>
<td>organic rich laminites</td>
<td>interbedded within or capping diamictite, contains diverse microfossil assemblage, probable Sourdough equivalent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sourdough limestone member-Kingston Peak Formation</td>
<td>Panamint Range (TM, PC, GW)</td>
<td>5 %e</td>
<td>5-10 m</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>flooding surface</td>
<td>weakly to strongly metamorphosed</td>
<td>organic rich laminites with anastomosing texture</td>
<td>restricted to the Panamint Range</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Noonday Dolomite</td>
<td>Nopah Range (NR) Winter's Pass Hills (WP)</td>
<td>4 %e</td>
<td>300+ m</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>flooding surface</td>
<td>normal to slightly reduced</td>
<td>minimal in chosen localities</td>
<td>tubes, seafloor ppt., sheet/crack cements, megadomes</td>
<td>passes laterally into deep water basinal facies (the Ibex Formation)</td>
<td></td>
</tr>
<tr>
<td>Rainstorm Member-Johnnie Formation</td>
<td>Alexander Hills (AH) Nopah Range (NR) Winters Pass Hills (WP)</td>
<td>&gt;10 %e</td>
<td>up to 100 m</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>flooding surface</td>
<td>less than 12</td>
<td>fabric retentive dol. (in odite) neomorphosed calcite (in fans)</td>
<td>formerly argonitic crystal fans</td>
<td>cutout along strike by major incision</td>
<td></td>
</tr>
<tr>
<td>middle Stirling Quartzite</td>
<td>Nopah Range (NR) Salt Spring Hills</td>
<td>6 %e</td>
<td>100 m</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>flooding surface</td>
<td>n/a</td>
<td>strongly recrystallized</td>
<td>none</td>
<td>contains Cloudina (Hagadorn and Fedo, 2000)</td>
<td></td>
</tr>
<tr>
<td>Lower Wood Canyon</td>
<td>Chicago Pass, Northern Nopah Range (CP) Boundary Canyon (BC)</td>
<td>4 %e</td>
<td>up to 100 m</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>highstand</td>
<td>n/a</td>
<td>minor fabric destructive dol.</td>
<td>none</td>
<td>Ediacaran fossils and the Precambrian-Cambrian boundary (C. pedum)</td>
<td></td>
</tr>
</tbody>
</table>

Figure 7. Summary of the key lithologic, paleontologic, and chemostratigraphic features of the Neoproterozoic Death Valley succession. Abbreviations: dol.—dolostone; ls.—limestone; ppt.—precipitate.
DEATH VALLEY NEO PROTEROZOIC CHEMOSTRATIGRAPHY

Figure 8. Chemostratigraphy of the Beck Spring Dolomite and preglacial Kingston Peak Formation (localities noted in text and Fig. 6). Where sampled, the basal 20 m records a negative to positive $\delta^{13}$C anomaly (repeated at several sections along strike); vsm—vase-shaped microfossil (cf. Melanocyrillium).

Figure 9. Chemostratigraphy of the glacial to postglacial Kingston Peak Formation and Noonday Dolomite (localities noted in text and Fig. 6). Data from Prave (1999) plotted for comparison. SDL—Sourdough limestone member; UNL—unnamed limestone; KPOnk—Thin oncolite bed in the Kingston Range.

Nopah Range: the section designated Nopah Range 2 contains the Johnnie oolite and Rainstorm Member carbonates, whereas a subsequent incision has removed these units from the Nopah Range 1 section. The $\delta^{13}$C values measured in thin dolomites in the lower and middle parts of the Johnnie Formation (many of them stromatolitic) remain negative ($\sim -3.5\%e$)—continuing the isotopic trend from the underlying Noonday beds—over a thickness of 200–300 m and across several significant sequence boundaries (Stewart, 1966, 1970). Above this interval, stromatolitic carbonates record a trend toward positive $\delta^{13}$C values, reaching a perigee of near $+3.5\%e$ near the contact with the Rainstorm Member.

Where not removed by incision, the Johnnie oolite, deposited during a flooding event atop a major sequence boundary (Summa, 1993), records a strong negative $\delta^{13}$C trend that declines up section from $-3.7\%e$ to $-7.1\%e$. Pink limestones several meters above the oolite (separated by green interference-ripple cross-laminated siltstones) display crude...
crystal fans and crystal layers, interpreted as former-aragonite seafloor cements (Fig. 4C). Over 100 m within the Nopah Range 2 section, these highly negative δ13C values decrease monotonically from −9.0‰ to −10.4‰. In the Winters Pass Hills section, the post-oolite carbonate beds are clastic and peloidal and trend from −9.1‰ to a nadir of −11.5‰; values return to ∼−9‰ at the Johnnie-Stirling contact.

In the Nopah Range 1 section, the Johnnie oolite and Rainstorm Member carbonates have been removed by incision and replaced by several beds of conglomerate and breccia interpreted as debris-flow deposits associated with incised-valley fill (Summa, 1993). Several clasts within the incised-valley fill are identifiable from underlying lithofacies (Beck Spring Dolomite giant ooids, Johnnie oolite, and lower Johnnie Formation stromatolites) and carry the isotopic fingerprint of their source. Above the debris flows, a monotonous sequence of featureless green and dark green shale extends up to the contact with the conglomerates of the overlying Stirling Quartzite. One thin carbonate unit, consisting of very finely laminated dark limestone, is present in this interval and records δ13C values between +2.6‰ and +2.9‰.

**Stirling Quartzite**

The Stirling Quartzite in Death Valley is predominantly nonmarine and contains few carbonate beds. The unit thickens to the west and records episodic marine incursions (Stewart, 1970). In the Nopah Range 1 section as well as in the Salt Spring Hills section (not plotted), the thin, possibly lagoonal, carbonates found throughout the middle part of the Stirling Quartzite record entirely negative δ13C values, but these become less negative up section (see footnote 1). The δ18O values of the middle Stirling Quartzite carbonates are highly depleted and suggest likely alteration. Farther to the west, marine carbonates in the overlying D member continue the positive trend, from −0.9‰ to +1.6‰ in the Boundary Canyon area and +0.1‰ to +1.6‰ at Bare Mountain (see footnote 1 and Corsetti and Hagadorn, 2000, respectively).

**Wood Canyon Formation**

Three prominent carbonate units are commonly exposed in the Lower Wood Canyon Formation (but the exact number varies from section to section) (Stewart, 1970; Diehl, 1979; Corsetti and Hagadorn, 2000). In the Boundary Canyon section, the lowest carbonates in the Lower Wood Canyon record isotopic values similar to those of the D member of the Stirling (+0.5‰) followed by a negative excursion (to an isotopic nadir of −4.4‰) (see footnote 1 and Corsetti and Hagadorn, 2000). The δ13C values of the uppermost carbonate return to mildly positive numbers (~+2.4‰). *Treptichnus pedum* is found below the last carbonate unit in the Boundary Canyon section in association with negative δ13C values, and arthropod scratch marks (cf. *Monomorphichnus*) are found above (Corsetti and Hagadorn, 2000). In the northern Nopah Range section at Chicago Pass, the lower two carbonate units record negative δ13C values, whereas the upper carbonate records a positive δ13C excursion. *Treptichnus pedum* is found in association with negative δ13C values between the second and third carbonate units, as in the Boundary Canyon area (Horodyski et al., 1994; Corsetti and Hagadorn, 2000; Hagadorn and Waggoner, 2000). Similar trends are noted in the equivalent White-Inyo facies to the northwest (Corsetti and Kaufman, 1994; Corsetti and Hagadorn, 2000).

The stratigraphic trends defined by well-preserved, closely spaced samples of Death Valley carbonates—duplicated at multiple sections—are accepted in this study to broadly reflect primary changes in ancient seawater. Furthermore, we recognize seven negative δ13C anomalies in a single stratigraphic succession constrained between the basal Beck Spring Dolomite (post−1.08 Ga) and the Precambrian/Cambrian boundary (Figs. 7, 11). Because negative δ13C anomalies are known to be associated with postglacial “cap” carbonates, the logical progression is to classify each of these potential geochemical events as primary or secondary and as glacial or non-glacial in origin. In the next section we outline the criteria used to evaluate the nature of each geochemical anomaly.

**ATTRIBUTES OF NEOPROTEROZOIC CAP CARBONATES**

The current state of Neoproterozoic correlation was outlined by Knoll (2000), who realized the ambiguities inherent in data sets from various continents. His task was difficult; lacking a high-resolution biostratigraphic framework and abundant reliable radiometric constraints, the subdivision of Neoproterozoic time—compared to more recent time intervals—is much more at the whim of personal bias and
basinal eccentricity. It is not surprising, then, that researchers sometimes have viewed the Neoproterozoic stratigraphic phenomena in their basin as a global model. The debate regarding the number of glaciations in Neoproterozoic time is a prime example of regional biases taking the global stage. One group, working primarily in Namibia, Svalbard, and Canada, sees more than two glaciations in the Neoproterozoic stratigraphic record (e.g., Kaufman et al., 1997a). Another group recorded very unusual seafloor precipitates and/or tube rock, with sheet cements and a negative δ13C anomaly that continued over a short vertical stratigraphic interval. A younger group recorded a rising limb of a spike over a significant stratigraphic interval. The shape of the negative δ13C anomaly recorded in the strata, however, is a function of the direction of secular change as well as the timing and rate of sediment accumulation and thus may be highly variable. It is possible that only the rising limb of a spike may be recorded in the rock record. Taken at face value, this limb might be considered a “positive excursion,” because the δ13C values start out negative and end up positive. However, recall that Neoproterozoic time is characterized by highly positive δ13C values only briefly punctuated by negative values. Thus, we consider any negative δ13C values to record a negative excursion, regardless of the actual shape or direction of the anomaly recorded in the stratigraphic record. Despite these controls, Kennedy et al. (1998) proposed that specific δ13C trends might be a diagnostic feature of cap carbonates. In some cases the δ13C values are ~0‰ or slightly negative immediately above diamictites and then fall to more negative values before ultimately returning to positive ones. In other organic-carbon–rich examples, the first preserved carbonate is strongly negative and trends toward positive δ13C values over a relatively short stratigraphic thickness. This variation suggests the possibility that cap-carbonate accumulation was initiated at different times across the basin and that these deposits are time-transgressive. In organic-carbon–poor cap carbonates, the δ13C values appear to start negative and continue to fall over a significantly larger stratigraphic thickness.

**Sequence Architecture**

Although postglacial rebound might obscure the absolute magnitude of sea-level change, all known cap carbonates are deposited on underlying glacial strata or a correlative hiatus. The cap carbonates are therefore deposited on a transgressive surface and appear to fill available accommodation space (Kennedy, 1996; Hoffman et al., 1998a). Recognition of known variations in sea level as recorded in the physical sedimentary record is thus central to our understanding of isotopic changes in the Neoproterozoic ocean.

**Stratigraphic Shape and Duration of the Negative δ13C Anomaly**

The δ13C composition of the oceans between ca. 750 Ma and ca. 590 Ma was, for the most part, highly positive (some δ13C values exceed +12‰) except for short negative spikes presumed to be associated with the glaciations (e.g., Kaufman et al., 1997a). We consider any primary negative δ13C values found in a stratigraphic succession deposited during this time interval (such as the Death Valley succession) to be “anomalous.” Note that a spike will have an initial positive-to-negative trend followed by a negative-to-positive trend.

Figure 11. Chemostratigraphic summary for the Death Valley succession. Seven negative anomalies are noted from the Beck Spring Dolomite to the Lower Wood Canyon Formation (four are associated with cap-carbonate-like features, and two actually rest upon glacial strata). The detailed analysis is found in Figure 7. Note that the two lower cap-like units contain “Sturtian-like” features, and the two upper cap-like units contain “Marinoan-like” features, as defined by Kennedy et al. (1998).
The Presence of Underlying Diamictite

This observation is the litmus test of the Kennedy et al. (1998) subdivision, as they do not consider any units that do not sit atop diamictites or unconformities that can be clearly correlated with glacial episodes (cf. Saylor et al., 1998).

CHARACTERIZATION OF NEOPROTEROZOIC BIOGEOCHEMICAL ANOMALIES IN DEATH VALLEY

Basal Beck Spring Dolomite

The basal Beck Spring Dolomite was deposited on the irregularly eroded uppermost Crystal Spring Formation (a sequence boundary, Mbuyi and Prave, 1993) and records at least 100 m of deeper-water facies that shoul to shallow depths, thus satisfying the flooding-surface criteria. These beds contain organic-carbon–rich lamine and rollup structures (Fig. 2A). Carbon isotope analyses reveal a slight negative excursion that returns to positive values of >10–15 m from the base of the formation. Although the basal Beck Spring Dolomite does not rest on a known glacial de- posit, it does sit above an unusual ferruginous sandstone interval in the upper Crystal Spring Formation at some localities.

Upper Beck Spring Dolomite

The carbonates recording the 10% negative excursion at the top of the Beck Spring Dolomite were deposited during a sea-level highstand and were eroded and affected by karst processes prior to Kingston Peak Formation deposition (Kenny and Kauth, 2001). These carbonates do not contain unusual carbonate fabrics. The negative δ13C excursion occurs in association with the karst, which has been inter- preted as a diagenetic artifact (Kenny and Kauth, 1992). It is notable, however, that the organic-carbon δ13C values generally co-vary with those of carbonate carbon, suggesting that this negative excursion records an oceanographic rather than diagenetic process (Kauf- man et al., 1997b). In addition, the negative excursion (recorded in samples microdrilled from nondiagenetic phases) starts nearly 100 m beneath the karstic surface (Halverson et al., 2002).

Sourdough Limestone Member

The deep-water Sourdough limestone member is in depositional contact with the glacial diamictites and coarse siliciclastic rocks of the lower part of the Kingston Peak Formation (Tucker, 1986) and thus constitutes a flooding surface. The Sourdough limestone member re- cords a negative δ13C excursion and a return to more positive δ13C values over a short stratigraphic interval. The limestone consists of a finely laminated organic-carbon–rich carbonate with possible rollup structures (Tucker, 1986). All of these features would suggest that the Sourdough limestone member is a cap carbonate (Prave, 1999).

Kingston Peak Oncolite Bed

This ~3 m bed sits atop diamicite of the Kingston Peak Formation. The negative anomaly at the base of the unit occurs in finely laminated carbonate. The δ13C values return to positive numbers within the overlying fossiliferous, oncolitic part of the unit (Awramik et al., 2000). The contact between the finely laminated lower part and the oncolitic part is sharp and possibly erosional. Note that we have sampled this unit stratigraphically at two sections along strike; thus, our data differ from previously published data (Kennedy et al., 2001a), which involved grab samples from the uppermost bed and not a stratigraphic iso- topic profile. Thus, the unit does contain some cap-carbonate characteristics (including the “litmus test” of an underlying glacial depos- it), although it appears to be sandwiched between two identical diamicite units.

The Noonday Dolomite

The Noonday Dolomite records a negative excursion that remains negative over a significant stratigraphic interval and includes unique tubular structures and cement fabrics nearly identical to those found in the Maier- berg Formation, Otavi Group, Namibia (Hoff- man et al., 1998b, 1998a). The Noonday Do- lomite rests in depositional contact on the Wildrose member diamicite in some areas and rests unconformably on the eroded remnants of various units of the underlying Palm- rump Group and basement rocks in other ar- eas. Thus, the Noonday Dolomite was deposited on a major flooding surface. These features, when combined, suggest that the Noonday Dolomite is a cap carbonate (Cor- setti, 1998; Prave, 1999; Corsetti et al., 2000).

The lower part of the overlying Johnnie Formation, separated from the upper Noonday Dolomite by a significant sequence boundary, records negative δ13C values, as well. This succession is predominantly siliciclastic, lend- ing a discontinuous nature to the chemostra- tigraphic profile. Thus, it is not possible to assess the completeness of the isotopic record through this interval. However, it is interesting to note that the negative δ13C values persist from the basal Noonday Dolomite through the lower part of the Johnnie Formation across a major sequence boundary and several minor sequence boundaries (Summa, 1993). Thus, the biogeochemical event may not be con- strained to a single depositional sequence, and “recovery” to more “normal” positive δ13C values in post-Noonday time may have been protracted.

The Rainstorm Member

The Johnnie oolite and the pink carbonates of the Rainstorm Member of the Johnnie For- mation record an intensely negative excursion during a flooding event above the base-of-oolite sequence boundary, but below a major incision surface. No glacial strata are currently known from directly below the Johnnie oolite. The oolite itself represents unusual carbonate precipitation, as it is the only carbonate bed in a predominantly siliciclastic succession and is extraordinarily laterally persistent. The pink limestones above the oolite display small crystal fans, in addition to a peloidal or clastic-carbonate texture in some sections (Fig. 4). These features, when combined, suggest that the oolite-precipitate carbonate is similar to cap-carbonate lithofacies, although these units do not rest on a known glacial deposit. We further note that these features are present be- low the incision that has been considered by others (e.g., Christie-Blick and Levy, 1989; Charlton et al., 1997; Abolins et al., 2000) to represent glacially driven sea-level drawdown during Marinoan glaciation. If this is so, it is possible that the Rainstorm Member carbon- ates record a preglacial negative trend in δ13C as seen in other sections around the world (Hoffman et al., 1998b; McKirdy et al., 2001), but the presence of unusual carbonate fabrics
The origin of the highly negative $\delta^{13}C$ values ($\sim -10\%$) is difficult to explain as a primary phenomenon without some sustained source of isotopically light carbon to the depositional basin. Similar events are recognized in broadly equivalent successions in Australia (Calver, 2000; McKirdy et al., 2001), Oman (Burns and Matter, 1993), and the Lesser Himalayas of India (Kaufman et al., 2000). Calver (2000) has explained these as the result of water-column stratification in a restricted basin, but this interpretation is inconsistent with the clearly open- and shallow-marine conditions recorded in the Johnnie Formation. Additional sources of $^{13}C$-depleted carbon are currently being considered (Kaufman and Corsetti, 2001); the thickness stratigraphic interval bearing the negative anomaly would seem to preclude a catastrophic methane release.

**Stirling Quartzite**

The thin lagoonal carbonates with negative $\delta^{13}C$ compositions in the middle part of the Stirling Quartzite also record highly depleted $\delta^{18}O$ values and probably do not reliably record original seawater compositions. They do occur on a flooding surface, but they do not contain other cap-carbonate features. Thus, there is no evidence that they represent a cap-carbonate lithofacies. In addition, they do contain poorly preserved *Cloudina* (Hagadorn and Waggner, 2000), one of the first weakly mineralized fossils, and thus postdate the interval commonly considered to contain glacial deposits.

**Lower Wood Canyon**

The negative anomaly in the Lower Wood Canyon Formation clearly brackets the Precambrian/Cambrian boundary and represents the boundary excursion seen in many sections around the world (e.g., Corsetti, 1998; Corsetti and Hagadorn, 2000).

**DISCUSSION AND IMPLICATIONS**

These comparisons suggest that the Death Valley succession records four biogeochemical events represented by carbonate $\delta^{13}C$ anomalies and carbonate textures analogous to those in Neoproterozoic cap carbonates; only two, however, are known to lie above recognized glacial deposits (Fig. 11). Each of these cap-like carbonates was deposited during a flooding event; thus, we cannot rule out the possibility that glacial strata have simply not been preserved along these hialal surfaces.

The situation is similar for the Maiberg cap carbonate from the Otavi Group in northern Namibia, which rests unconformably on the underlying Ombaatjie Formation platform carbonates in proximal settings and on thick glacial diamictites of the Ghaub Formation in basinward settings (Hoffman et al., 1998a, 1998b). In the platform setting, the Ghaub glaciation is represented (except in rare instances) by a disconformity. Therefore, although we can confirm the occurrence of four negative excursions in strata with cap-carbonate-like features, we cannot rule out the existence of at least four glaciations in Neoproterozoic time.

Alternatively, some other, nonglacial process may control the occurrence of negative $\delta^{13}C$ anomalies and cap-carbonate-like lithofacies. For example, Grotzinger and Knoll (1995) and Knoll et al. (1996) hypothesized that intense ocean stratification, with concomitant buildup of alkalinity via sulfate reduction and $\delta^{13}C$ depletion in anoxic deep waters, might be responsible for the observable features. It is unclear, however, whether enough alkalinity could be delivered from (presumably) one overturn event to precipitate such widespread cap carbonates. In this scenario, cap carbonates and $\delta^{13}C$ anomalies need not be unquestionably linked to glaciation.

The two older “events” preserved in Death Valley record features similar to Sturtian-style cap carbonates (the basal Beck Spring Dolomite and the Sourdough limestone member of the Kingston Peak Formation), whereas the two younger ones record features similar to Marinoan-style (or Varangian) cap carbonates (the Noonday Dolomite and the Rainstorm Member of the Johnnie Formation) as defined by Kennedy et al. (1998). PAUP analysis can be used to highlight the similarity (or difference) between character sets, but it cannot be used to imply temporal information as has been inappropriately done in this debate. Thus, an equally parsimonious way to interpret the data would be to call upon some, or all, of the sister groups (the individual cap carbonates) to represent separate events. Hypothetically, this interpretation could mean the possibility of many separate Sturtian-style events and many separate Marinoan-style events (a cheemostratigrapher’s nightmare). We think that our data support the existence of at least two Sturtian-style events and two Marinoan-style events in one continuous section, thus demonstrating the pitfall in using PAUP analysis to bring temporal information to this debate. Although we can comment on the number of cap-carbonate-like units in Neoproterozoic time, the Death Valley succession is too poorly dated to resolve the timing of these events, and the terms “Sturtian-style” and “Marinoan-style” simply are used for comparison, not to imply age control.

Although certain carbonate lithofacies, commonly interpreted to have formed in deeper water (e.g., Kennedy, 1996), characterize Neoproterozoic cap carbonates worldwide (as already discussed), they are not unique to these units, and other lithofacies and geochemical indicators appear possible. For example, the Johnnie oolite fits several of the cap-carbonate criteria but does not represent a traditional cap-carbonate lithofacies. The $2$–$3$-m-thick oolite unit can be traced continuously over $16,000$ km$^2$ in the Great Basin and is also similarly widespread in the Neoproterozoic succession in Caborca, Mexico (Stewart, 1970; Stewart et al., 1984). It is an extraordinarily widespread carbonate unit within a predominantly siliciclastic succession and may represent a unique cap-carbonate lithofacies in which the biogeochemical anomaly is manifested in shallow-water, agitated environments. Shallow-water facies have been described from the Egan Formation, Kimberley region, Western Australia, known to cap glacial units and record negative $\delta^{13}C$ values (Corkeron and George, 2001). It is interesting to note that these units are thought to record a post-Marinoan glacial episode (Grey and Corkeron, 1998), thus adding to the known number of Neoproterozoic glaciations in Australia. Shallow-water cap-carbonate facies are also known from Mauritania (Deynoux et al., 1976).

The basal Beck Spring Dolomite, the Sourdough limestone member, and the crystal-fan beds of the Rainstorm Member of the Johnnie Formation all record strongly enriched $^{13}C$ compositions of organic carbon relative to the $\delta^{13}C$ values in carbonate beds above and below (e.g., the $\Delta^{13}C$, or $\delta^{13}C_{carbonate} - \delta^{13}C_{organic}$, is reduced). The process responsible for these low $\Delta^{13}C$ values is unknown. However, in the modern ocean, the introduction of micromutrients (e.g., iron) causes a reduction in $^{13}C$ of corresponding organic matter; as growth rates increase in response to the influx of nutrients, carbon becomes limiting and biogenic isotopic discrimination (commonly $\sim 20\%$–$30\%$) decreases (Bidigare et al., 1997, 1999). Neoproterozoic postglacial oceans are predicted to contain an abundance of dissolved iron and other nutrients; the reduced $\Delta^{13}C$ may reflect this prediction (Kaufman et al., 1997a; Hayes et al., 1999).
CONCLUSION

The correlation of Neoproterozoic strata is difficult, and therefore the ability to determine the tempo of evolutionary events recorded in Neoproterozoic strata is restricted. We acknowledge that the Death Valley succession may not be as well preserved, dated, or structurally simple as other Neoproterozoic sections around the world. But as originally recognized by Cloud (1973), the Death Valley section, arguably one of the most accessible and intensely studied in the world, does contain many of the key geologic features that characterize Neoproterozoic time. This study confirms the presence of multiple negative δ13C excursions throughout the Neoproterozoic. Two of these are associated with known global glaciations, but at least two others are associated with cap-carbonate lithofacies lacking the underlying diamicrite. This circumstance indicates either that more than two glaciations occurred in Neoproterozoic time or that negative excursions and cap-carbonate lithofacies are the result of other oceanographic perturbations, which may be independent of glacial phenomena.

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CORSETTI and KAUFMAN

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