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Latest Devonian (Famennian) global events in western Laurentia: Variations in the carbon isotopic record linked to diagenetic alteration below regionally extensive unconformities

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ABSTRACT

Integrated analysis of the sedimentology, stratigraphy, and chemostratigraphy of the uppermost Devonian Chaffee Group of Colorado reveals the presence of two regionally extensive unconformity surfaces associated with globally recognized extinction/eustatic events. The contact between semi-restricted, marginal marine, mixed siliciclastic–carbonate deposits of the Parting Formation and open marine carbonate of the Dyer Formation is a major marine flooding surface across western Colorado. This flooding surface rests at the top of an ~5 m thick, transgressive, cross-bedded, shoreline sandstone unit that locally overlies a 2.5-m-thick paleokarst breccia. $\delta^{13}C$ values shift lighter across the formation contact, in some cases by as much as 5‰. Oxygen isotopic values are extremely variable between measured stratigraphic sections, in cases invariant across the contact, and in other cases covarying with the $\delta^{13}C$ values. At Ouray, CO, $\delta^{18}O$ covaries with $\delta^{13}C$ throughout the section, and reaches extreme values (<-30‰) below the unconformity. An isotopic shift in rocks of this age in Utah, coined ALFIE, was previously correlated to the Parting–Dyer contact. This study demonstrates that the carbon and oxygen isotopic record of ALFIE is highly variable across western Laurentia, and that important carbonate chemostratigraphic variations result from diagenesis that is clearly linked to a regional unconformity and associated relative sea-level fall. This lowstand may be a signal of eustatic fall associated with the Dasberg Event, a late Famennian marine extinction event. Similar isotopic patterns exist for strata below and above a paleokarst breccia in the upper Dyer Formation that we link to the globally significant latest Famennian Hangenberg Event, which includes a eustatic lowstand and subsequent transgression. Similar to the Parting–Dyer contact, both carbon and oxygen isotopes in strata below this regional unconformity surface show the variable nature of diagenetic alteration of carbonate units during lowstand conditions. Our data also suggest that correlatable $\delta^{13}C$ chemostratigraphic shifts can be diagenetically produced during lowstands across a regionally widespread (western U.S.) basin, and that these $\delta^{13}C$ shifts may be expressed within outcrops that show no macroscopic sedimentological signature of subaerial exposure. This has broad implications for the evaluation of $\delta^{13}C$ data in the rock record, particularly the assumption that extensive correlatable isotopic anomalies reflect global marine signatures.

1. Introduction

The Devonian–Carboniferous boundary interval records major changes in the ocean and atmosphere, including mass extinctions, glaciations, changes in sea level, episodes of oceanic anoxia, and large marine carbon isotopic shifts (Walliser, 1984; Johnson et al., 1985; Streel et al., 2000; Joachimski and Buggisch, 2002; Sandberg et al., 2002; Brand et al., 2004; Buggisch and Joachimski, 2006; Kaiser et al., 2006; Cramer et al., 2008; Kaiser et al., 2008). Many of these processes were dynamically linked. For instance, it has been hypothesized that climatic cooling, due in part to terrestrial plant radiation (Algeo et al., 1995; Algeo and Scheckler, 1998; Caplan and Bustin, 1999; Streel et al., 2000; Algeo, 2004), led to the onset of southern hemisphere glaciation, which in turn induced a major sea level fall (Caputo and Crowell, 1985; Isaacson et al., 1999; Streel et al., 2000; Sandberg et al., 2002; Isaacson et al., 2008). Extensive oceanic anoxia in this interval led to

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widespread deposition of organic rich black shale (Berry and Wilde, 1978; House, 1985; Becker, 1993a; Caplan and Bustin, 1999; Kump et al., 2005) and biotic crises, which in turn produced significant changes in the isotopic values of the dissolved inorganic carbon reservoir ($\delta^{13}C$).

Two significant events in this interval include the Dasberg and Hangenberg Events, which were first described from central Europe, but are now more globally recognized. The Dasberg Event is a multi-stage event recorded in strata of the Lower *expansa* conodont Zone of the upper Famennian. It is characterized by a sea level fall, the development of an unconformity, and subsequent deposition of transgressive black shale lithofacies (Becker, 1993a; Sandberg et al., 2002; Kaiser et al., 2006, 2009; Hartenfels and Becker, 2009). These events were coincident with the extinction of marine fauna, particularly ammonoids (e.g., Hartenfels and Becker, 2009). No significant $\delta^{13}C$ excursion is associated with the Dasberg Event in either Europe or Morocco (Kaiser, 2005; Buggisch and Joachimski, 2006; Hartenfels and Becker, 2007; Kaiser et al., 2008).

The latest Famennian Hangenberg Event is also defined by multiple eustatic changes (Ziegler and Sandberg, 1984; Caputo, 1985; Johnson et al., 1985; Bless et al., 1993; Becker, 1996; House, 2002; Sandberg et al., 2002; Kaiser et al., 2009; Myrow et al., 2011), the widespread deposition of black shale (Caplan and Bustin, 1999; House, 2002; Kaiser et al., 2006, 2009), and marine extinctions (Becker, 1996; Olempska, 1997; Sallan and Coates, 2010). In contrast to the Dasberg Event, the Hangenberg Event produced excursions in the $^{87}Sr/^{86}Sr$ and $\delta^{13}C$ isotopic records (Kürschner et al., 1993; Brand et al., 2004; Buggisch and Joachimski, 2006; Kaiser et al., 2006; Cramer et al., 2008). For instance, a positive $\delta^{13}C$ excursion that begins in the Upper *expansa* conodont Zone reaches peak values between ~+3 and +7‰ (VPDB) in the Upper *praesulcata* Zone (Brand et al., 2004; Buggisch and Joachimski, 2006; Kaiser et al., 2006; Cramer et al., 2008; Kaiser et al., 2008; Matya et al., 2010). Marine faunal extinction and a similar magnitude $\delta^{13}C$ positive isotopic anomaly associated with the Hangenberg Event have been recognized in North America (Gutschick and Sandberg, 1991; Becker, 1993b; Streel et al., 2000; Sandberg et al., 2002; Brand et al., 2004; Cramer et al., 2008; Myrow et al., 2011).

Myrow et al. (2011) presented high-resolution sedimentological, lithostratigraphic, and carbon isotope chemostratigraphic data for three latest Famennian sections in the western United States, two of which are in Utah, and one in western Colorado. These sections span conodont biozones correlative to the Dasberg and Hangenberg Events. Within these strata, a major shift from negative to positive $\delta^{13}C$ values was correlated to the Dasberg Event and coined ALFIE (A Late Famennian Isotope Excursion). The origin of this $\delta^{13}C$ shift, and the reason for its apparent absence in Europe and Morocco, remains unresolved. Myrow et al. (2011) speculated that ALFIE was (1) a global shallow marine phenomenon not recorded in deep water European sections, (2) a result of Laurentian epicratonic seas temporarily drifting geochemically away from global secular isotopic values, or (3) the result of regional diagenesis. A younger $\delta^{13}C$ shift, recorded in strata in Glenwood Canyon, CO, was considered a record of the Hangenberg Event, evidenced by a negative shift in isotopes below a conspicuous paleokarst interval and a pronounced positive excursion in overlying open marine strata.

Herein, we report sedimentological, stratigraphic, and chemostratigraphic data for additional outcrops of the Devonian Chaffee Group in west-central and southwest Colorado that also record the Dasberg and Hangenberg Events. We document the regional sedimentological and sequence stratigraphic framework of these deposits, in conjunction with new carbon isotopic data, to resolve the origin of the Dasberg-associated carbon isotopic excursion ALFIE. In addition, we provide further documentation for the presence of the Hangenberg Event across Laurentia. Finally, we examine the potential for meteoric and basinal fluids to diagenetically produce regionally extensive shifts in $\delta^{13}C$, and explore how this mechanism influences the general interpretation of $\delta^{13}C$ variations in the rock record.

2. Location and methods

The Chaffee Group outcrops described in this study are located in west-central and southwest Colorado (Fig. 1). Exposures are found at Cement Creek, approximately eight miles southeast of Crested Butte, Colorado, and about three miles east from the intersection of Highway 135 and CR 740 on the north side of the creek. A second exposure of the Chaffee Group is located in Box Cañon Falls Park, in the town of Ouray. A third site is at an abandoned quarry in the town of Rockwood, ~17 miles north of Durango. Lastly, a section of these strata are exposed north of the town of Gilman, on the east wall of the Eagle River canyon.

Stratigraphic sections were measured on a bed-by-bed manner and carbonate samples were generally collected at 0.2–0.5 m spacing throughout where lithologies permitted. Sets of samples from some outcrops were powdered from whole rock after removal of weathered surfaces and conspicuous veins with a trim saw. Later samples were cut and microdrilled with a dental drill bit. Powders were analyzed at Saint Louis University (SLU) with a Phillips PW 1830 X-ray Diffraction instrument to determine the weight percent of calcite versus dolomite, and to detect any insoluble siliciclastic sediment.

Carbonate carbon and oxygen analyses were performed at both SLU and at Washington University (WU) on powdered whole-rock carbonate samples. The SLU analyses were treated with 100% H_3PO_4 at 50 °C to liberate CO_2. The carbon and oxygen isotope compositions of the CO_2 were measured in a Micromass Isoprime isotope ratio magnetic sector (IRMS) mass spectrometer using continuous flow methods. The resultant $\delta^{13}C$ and $\delta^{18}O$ values were established through in-house standards referenced to the NIST NBS-19 standard. At WU, powders were reacted for 4 h at 72 °C with an excess of 100% H_3PO_4 in He-flushed, sealed tubes. Evolved CO_2 was sampled with a Thermo Scientific Gas Bench II, and isotopic ratios were measured with a Thermo Scientific Delta V Plus. Isotopic measurements were calibrated against NBS-19, NBS-20, and two in-house standards, with analytical errors of <0.1‰ (1σ) for $\delta^{13}C_{carb}$ and <0.2‰ (1σ) for $\delta^{18}O_{carb}$. All isotopic values are expressed in per mil (‰) notation on the VPDB scale.

3. Chaffee Group

The late Famennian Chaffee Group of west and central Colorado consists of two formations, the mixed siliciclastic and carbonate Parting Formation, and the overlying carbonate Dyer Formation (Behre, 1932; Lovering and Johnson, 1933; Johnson, 1934; Tweto, 1949; Bass and Northrop, 1953; Campbell, 1970; Tweto and Lovering, 1977). The Parting

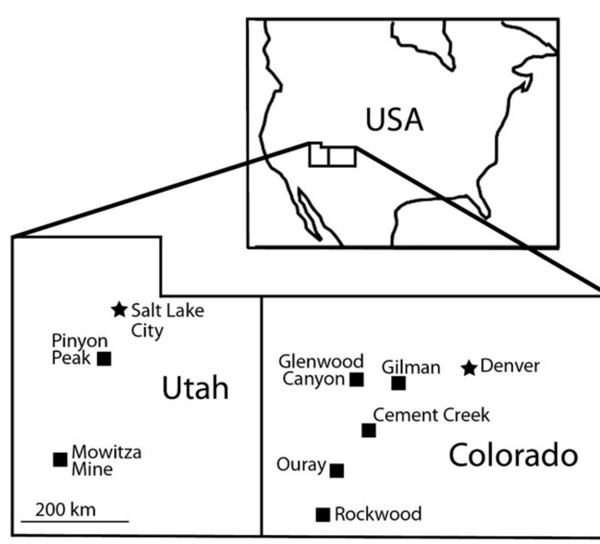


Fig. 1. Location map for sections in western U.S. Stars show locations of nearby cities, and squares are field sites.

consists of a basal, transgressive, cross-bedded quartz sandstone, and a diverse suite of overlying lithofacies, including organic-rich black shale, siltstone, quartz sandstone, micritic limestone, and stromatolitic dolostone. The overlying carbonate of the Dyer Formation is further subdivided into the fossiliferous Broken Rib Member and predominantly dolomitic Coffee Pot Member (Campbell, 1970). Myrow et al. (2011) provide a detailed measured section, sedimentological description, and chemostratigraphic data for the Chaffee Group at Glenwood Canyon, west-central Colorado.

3.1. Parting Formation

At Cement Creek, the Parting Formation (Fig. 2) consists of 25.2 m of interbedded marl, carbonate mudstone, dolograinstone, sandstone, and minor shale. A basal, 77 cm thick, medium to coarse-grained sandstone rests directly on the underlying Ordovician Fremont Limestone (Johnson, 1944). The overlying strata are more carbonate rich than most exposures of the Parting, including the well-known exposures in Glenwood Canyon of nearly identical thickness (25.8 m) (Myrow et al., 2011). At Cement Creek, the Parting is dominated by ribbon-bedded dolomudstone, which makes up units up to 4.5 m thick. Locally, the dolomudstone contains floating medium-size quartz grains that comprise as much as 15% of the rock. Minor, thin (<10 cm) dolograinstone and shale beds are present, the latter of which decrease in abundance upsection. Marl beds range from 4 to 34 cm thick, are variable in color, and are interbedded with the dolomudstone. At 9.48 m in the section, there is a 4.45 m thick regional marker bed composed of bright-white-weathering, massive, carbonate mudstone.

A few meters above this bed, at 16.25 m, there is a 2.6 m thick interval that consists in ascending order of: 1.18 m of karst breccia (Fig. 2B), 0.75–1.12 m of massive dolosiltite, 1–10 cm of red shale, 20–52 cm of dolosiltite with paleokarst cavities (Fig. 2C), and 1–5 cm of red and pink carbonate mudstone. The breccia at the base of this interval has a pink, silty matrix, fitted fabrics, and vugs with sparry calcite cement. The upper dolosiltite is massive, tan to pink, highly variable in thickness, and the karst cavities are filled with bioclastic wackestone with very thin fossil fragments (Fig. 2A). The red/pink carbonate mudstone contains rounded, micritic intraclasts with abundant borings.

The top of this interval, at 18.85 m, marks an abrupt facies change to a 6.34 m thick unit of white-weathering quartz sandstone that caps the formation (Fig. 2A). The basal 1.9 m of the sandstone is cross-bedded (Fig. 2F), very thin to thin bedded (5–12 cm), very-coarse- to coarse-grained, and locally contains abundant intraclasts. The overlying 2.35 m is finer grained and has 1–7 cm thick, ripple cross-laminated beds with a few horizontal burrows. The uppermost 2.09 m of the sandstone unit consists of 10–30 cm thick very-coarse- to coarse-grained sandstone beds. A stratigraphically correlative bed at Glenwood Canyon (4.78 m thick) contains trace fossils, including abundant *Skolithos* burrows.

The Parting Formation at Ouray (Fig. 3) is 10.1 m thick, and includes a 19–29 cm thick, basal quartz sandstone that overlies an irregular Precambrian basement surface. The sandstone consists of poorly sorted, coarse- to very-coarse-grained sandstone with isolated pebbles up to 16 mm in diameter. Interbedded carbonate mudstone, siltstone, shale, and marl with abundant halite casts overlie this basal sandstone. Strata from 1.5 to 2.7 m are dominated by red shale and burrow-mottled siltstone. At 2.7 m there is a sharp transition to a 78 cm thick, fine- to medium-grained, brown weathering, laminated sandstone bed, followed by a sharp transition to carbonate-dominated strata. The carbonate interval is composed of medium to thick beds of brown to light gray, coarse grainstone, the basal part of which displays an upward decrease in isolated coarse to fine quartz sand grains from nearly 50% to <5% of the rock volume. At 6.72 m there is a 20 cm thick bed of brown, dolomite cemented, very coarse- to coarse-grained, quartz sandstone. This is overlain by a 3.17 m thick, white-weathering, and massive dolomudstone (Fig. 3) with a mottled fabric and fenestrae. The bed, which caps the Parting Formation, is very similar to the white-weathering bed at 9.48 m in the Cement Creek section, the top of which lies a few meters below the paleokarst breccia (Fig. 6).

The basal unit of the Chaffee Group at Gilman consists of 3.92 m of granular conglomerate and minor, trough cross-bedded sandstone with very angular quartz grains (Fig. 4A, B). We ascribe this basal unit, and an overlying 1.45 m thick unit of silica- and carbonate-cemented sandstone, to the Parting Formation. The section at Rockwood does not include exposure of the Parting Formation.

3.2. Parting Formation: interpretation

The basal quartz sandstone beds at Cement Creek and Ouray are examples of thin transgressive sandstone deposits. Shoreline reworking by shallow-marine processes resulted in the winnowing of mud and the deposition of texturally and compositionally mature sandstone atop an unconformity surface. This sub-Devonian unconformity extends across the state of Colorado (Johnson, 1934, 1944; Myrow et al., 2003). Whereas the basal sandstone of the Parting rests directly on Precambrian basement at Ouray, at nearly all other localities in Colorado it rests on older Paleozoic sedimentary units (Johnson, 1934, 1944; Myrow et al., 2003). In these localities, quartz sand was transported some distance to the site of deposition during development of the underlying disconformity and then reworked by the transgressing Late Devonian sea.

The mixed siliciclastic–carbonate facies of the Parting Formation at Glenwood Canyon include organic-rich dark gray to black shale; sandstone; dark, organic-rich marl and carbonate mudstone; and minor dolomitic stromatolite beds. These lithofacies were previously interpreted to represent deposition in restricted, marginal marine environments that were occasionally hypersaline and, at other times, dysaerobic to anaerobic (Myrow et al., 2011). The lower 3.48 m of the Ouray section has similar lithofacies and sedimentary structures as Glenwood Canyon, including halite casts, although the red shale at Ouray suggests oxic water and/or sediment column conditions.

In contrast to the Glenwood Canyon section, at Cement Creek the Parting lacks halite casts and contains more carbonate-rich facies, which indicate an offshore marine depositional environment. The interbedding of shale and carbonate mudstone reflects episodic cessation of carbonate production by siliciclastic mud delivered from distal fluvial systems. The massive, white-weathering carbonate mudstone bed, which defines the top of the formation at Ouray, is tentatively correlated to the bed of similar character at 9.48 m in the upper Parting at Cement Creek. Evidence for subaerial exposure—in the form of paleokarst breccia and cavities within mudstone in strata above this bed at Cement Creek—suggests that the top of the white bed at Ouray may represent a diastem. The paleokarst breccia at Cement Creek records dissolution of carbonate rock by meteoric water (Esteban and Klappa, 1983) and subsequent collapse. Possible reworking of the upper surface of the paleokarst breccia, and subsequent deposition of carbonate with karst cavities, reflects both a relative sea level rise and a second period of subaerial exposure just prior to sandstone deposition.

At Cement Creek, the abrupt lithofacies change from paleokarsted carbonate to the thick, white, trough cross-bedded, quartz sandstone suggests passage of a transgressing shallow-marine shoreline setting. Stacked, medium-scale cross-bed sets with uniform dip orientations are interpreted as migrating dune deposits. Combined with the presence of horizontal burrows at this locality, and abundant *Skolithos* burrows at Glenwood Canyon (Myrow et al., 2011), supports the interpretation of a shoreface depositional environment. Thus, the base of the sandstone marks a regional combined lowstand exposure surface and marine flooding surface. Evidence for karstic dissolution is not present at Glenwood Canyon, and neither the karst nor the transgressive sandstone is present within the Ouray section. However, given the record of regional relative sea level fall and extensive karst development between the white bed and sandstone at Cement Creek, we correlate the top of the white bed at the top of the Parting Formation at Ouray to this same lowstand surface. The bright white color and absence of textures in the carbonate below this surface may reflect diagenetic alteration during exposure. Upward fining and thinning of the sandstone unit at Cement Creek reflects deepening across the shoreface during shoreline retreat.

The Parting Formation at Gilman is anomalous relative to other sections in Colorado. These deposits comprise a thin interval of quartz conglomerate and sandstone, and are thus compositionally mature. The large grain size indicates a relatively high-energy environment, although the lack of sedimentary and biogenic structures makes it difficult to discern if these are fluvial or marginal marine strata. In either case, the grain size also suggests deposition in proximity to energetic river systems, which in this case may have been close to the Homestake Shear Zone, a structural feature that was reactivated multiple times in the Precambrian, and later in the Phanerozoic, and may have played a role in the distribution and thickness of Paleozoic units (Myrow et al., 2003; Allen, 2004).

3.3. Dyer Formation

At Cement Creek, the lower 6.95 m of the Broken Rib Member of the Dyer Formation, which rests directly on the quartz sandstone at the top of the Parting Formation, consists of pink weathering, bioturbated lime wackestone. It contains ~15–30% fossil fragments, most of which are small (<1–2 mm) disarticulated shells dispersed in mudstone. Fossils include rugose corals and crinoid ossicles, both of which are more common in the lower half of the member. There are no other primary sedimentary structures in this unit, including any obvious lamination. The rest of the Dyer at Cement Creek, assigned to the Coffee Pot Member, is dominated by tan, laminated dolograinstone. Parallel lamination and low-angle, near parallel lamination are abundant, and locally there is cryptic stromatolitic lamination. Minor cm-thick chert beds are present between 40 and 41 m.

An interval of anomalous carbonate facies exists between 45.86 and 51.65 m (Fig. 6). At the base is a 1.57 m thick interval that consists of a lower 57 cm thick paleokarst breccia and an overlying meter of white carbonate mudstone with breccia-filled paleokarst pockets. The breccia is brown weathering with fitted fabrics and cement-filled cavities. Paleokarst pockets in the overlying mudstone contain small mudstone clasts and pink siltstone matrix. Two beds (23 and 46 cm thick) of fine dolograinstone with mm-scale, cement-filled vugs directly overlie these deposits. This is followed by 1.42 m of thin beds of dolosiltite with fenestrae, a 24 cm thick bed of intraclast conglomerate, and fine-grained dolograinstone with minor intraclasts. The next interval, above 49.59 m, consists of 1.5 m of cover, 34 cm of dolomudstone and shale, and 22 cm of gray-white, coarse-grained, silica-cemented quartz sandstone. This ~2 m thick interval was traced laterally for approximately 400 m along strike, where it consists entirely of fine- to medium-grained sandstone with trough cross-bed sets up to 55 cm thick. Paleokarst breccia with coarse sandstone matrix is also sporadically exposed in this interval along strike (Fig. 2E).

The overlying 3.31 m consists of an unusual succession of lithofacies that include blue-weathering, silicified fine-grained grainstone; highly altered, brittlely deformed marl and slightly discordant thin-bedded fine grainstone; and a 44–78 cm thick bed of oncolites with carbonate mudstone intraclasts, with a highly irregular base. The top of this interval has a 7 cm thick marl bed with scattered medium quartz sand grains. The rest of the formation (14.04 m) consists of poorly exposed, ribbon-bedded, carbonate mudstone with 1–12 cm thick beds. The formation is directly overlain by poorly exposed, tan weathering, medium-grained quartz sandstone of the Mississippian Gilman Sandstone. Along strike, the upper 5–6 m of the ribbon bedded facies of the Dyer contains meter-scale pockets of coarse calcite cement with angular clasts. These irregular, paleokarst cavities are also infilled with quartz sandstone close to the upper contact of the formation (Fig. 4D).

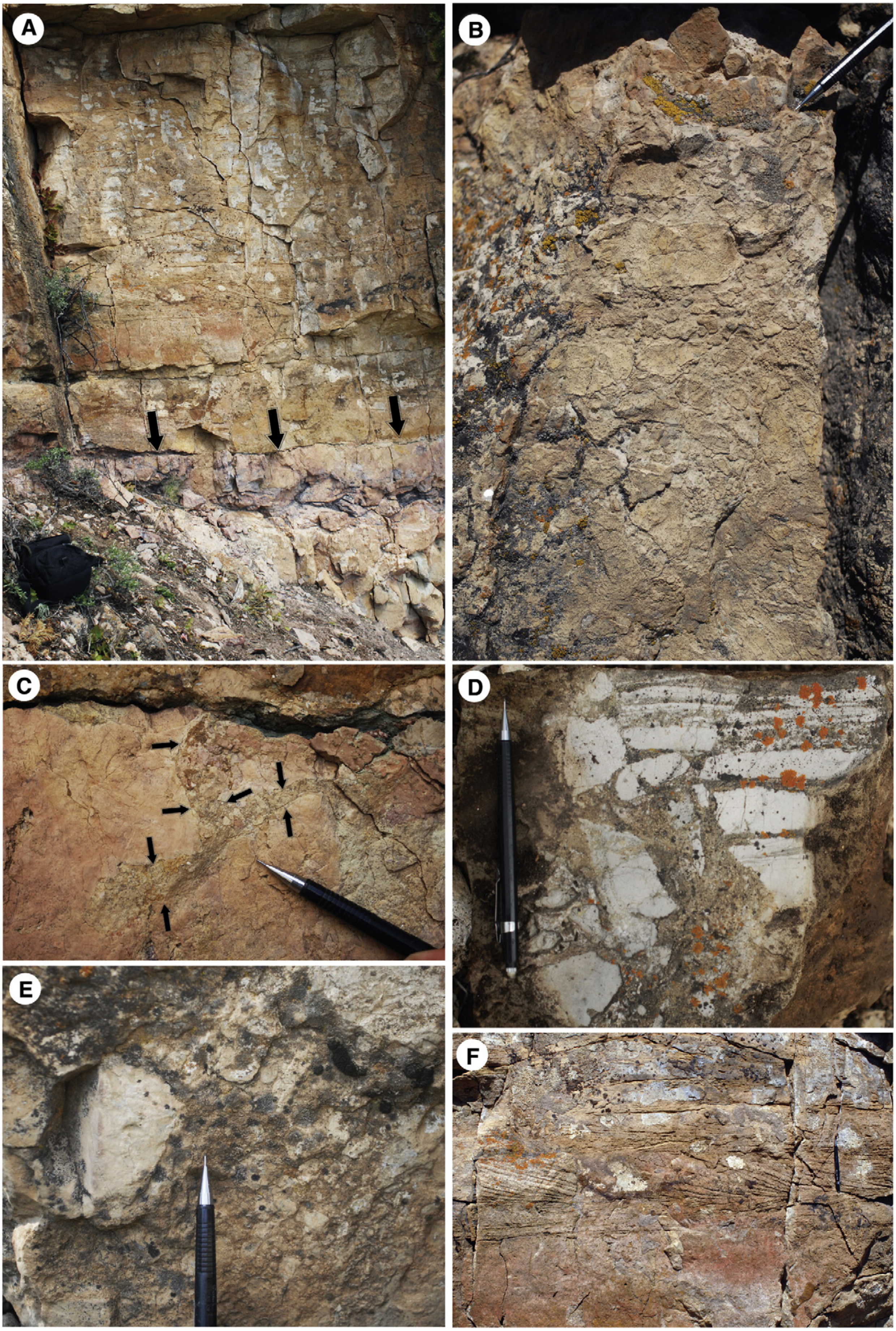
At Ouray, the basal unit of the Dyer Formation consists of more than 10 m of tabular, medium bedded, gray-brown, fine-grained grainstone. The succession is quite homogeneous, except for a single 8 cm thick bed of dark gray shale at 14.06 m.

At Rockwood, the lower part of the Chaffee Group is not exposed, and the section begins in the upper part of the Dyer Formation. The base of this section consists of coarse- to very-coarse-grained, light gray to pink, grainstone with <3% medium to very coarse quartz sand grains. At 2 m there is a shift to fine grainstone with no quartz sand. At 3.75 m, there is a 94 cm thick unit of red and white stained nodular limestone with cement-filled vugs, which is capped by fine grainstone. At 9.5 m there is a 2.6 m interval of large, cobble- to boulder-sized, irregularly shaped, sub-rounded pseudoclasts of identical composition to the underlying fine grainstone (Fig. 5). This "conglomerate" is gradational upwards from undisturbed underlying grainstone through ~50 cm of partly discontinuous bedding. The matrix of this psuedoconglomerate is of similar composition, but also contains minor iron-rich shale (Armstrong and Mamet, 1976). The upper 30 cm of this unit is intensely weathered, and the top is marked by a sharp surface. The uppermost part of the section consists of recessive dark gray carbonate mudstone, black mudstone, and ribbon bedded calcisiltite, similar to the upper Coffee Pot Member at Cement Creek. We place the contact with overlying Mississippian Leadville Limestone strata is at 13.62 m in the section, at which level Armstrong and Mamet (1976, p. 5) recovered a fauna that they considered "Late Devonian or Mississippian". A Late Tournaisian (lowermost Mississippian) fauna was recovered 13.4 m above this level in the Leadville (Armstrong and Mamet, 1976).

At the Gilman section, carbonate deposits with minor shale, siltstone, and marl beds overlies the Parting Sandstone strata. Predominant facies include nodular to ribbon-bedded dolomudstone, dolosiltite, fine to coarse-grained grainstone, flat-pebble conglomerate, and stromatolite (Fig. 4D,E). Cherty mudstone and fine grainstone beds are locally abundant in the upper part of the section. The section is punctuated by a series of paleokarst horizons, some of which include irregular pockets of breccia, red siltstone, and sandstone. Above 8.75 m, beds of blue dolomudstone contain 1–3 cm thick lenses of fine- to medium-grained quartz sandstone, and from 9.15 to 9.29 m there is the stratigraphically lowest karst breccia of the section with dispersed fine to medium grained quartz sand grains (Fig. 4C). At 9.29 m there is another thin interval (34 cm) with irregular lenses of paleokarst breccia within dolomudstone beds. The interval from 10.89 to 14.08 m contains a wide variety of paleokarst features, as well as possible gypsum pseudomorphs. There is also a possible paleosol at 11.94 m that consists of fitted fabrics of dolomudstone and intervening green marl with small carbonate nodules. This surface is overlain by over 80 cm of paleokarst breccia that filled cavities with large clasts, including those of partially displaced bedding.

Sandstone intervals in the Gilman section include a 5 cm thick bed of fine- to coarse-sandstone at 16.8 m, which is overlain by a 9 cm thick bed of dolograinstone with 1–2% floating medium to coarse quartz sand grains. At 17.74 a coarse sandstone bed 4–6 cm thick contains grains up to 2 mm diameter. From 24.02 to 25.44 m, at the top of the section below the Mississippian Gilman Sandstone, there are

Fig. 2. Cement Creek, CO. (A) Parting Formation. Black arrows point to top of paleokarst interval and base of upper Parting Sandstone at 19.85 m. Camera case for scale. (B) Paleokarst at 16.25 m with irregular angular carbonate clasts in red siltstone matrix. (C) Micro-paleokarst at 18.61, directly below upper Parting Sandstone. (D) Paleokarst breccia at base of Mississippian Gilman Sandstone. Carbonate mudstone clasts are surrounded by very coarse quartz sandstone. (E) Paleokarst with coarse sandstone matrix in the 46–51 m interval. (F) Cross-bedding in upper Parting Sandstone at 19 m. Photos B–F: pencil for scale is 14 cm long; tip is 2 cm long.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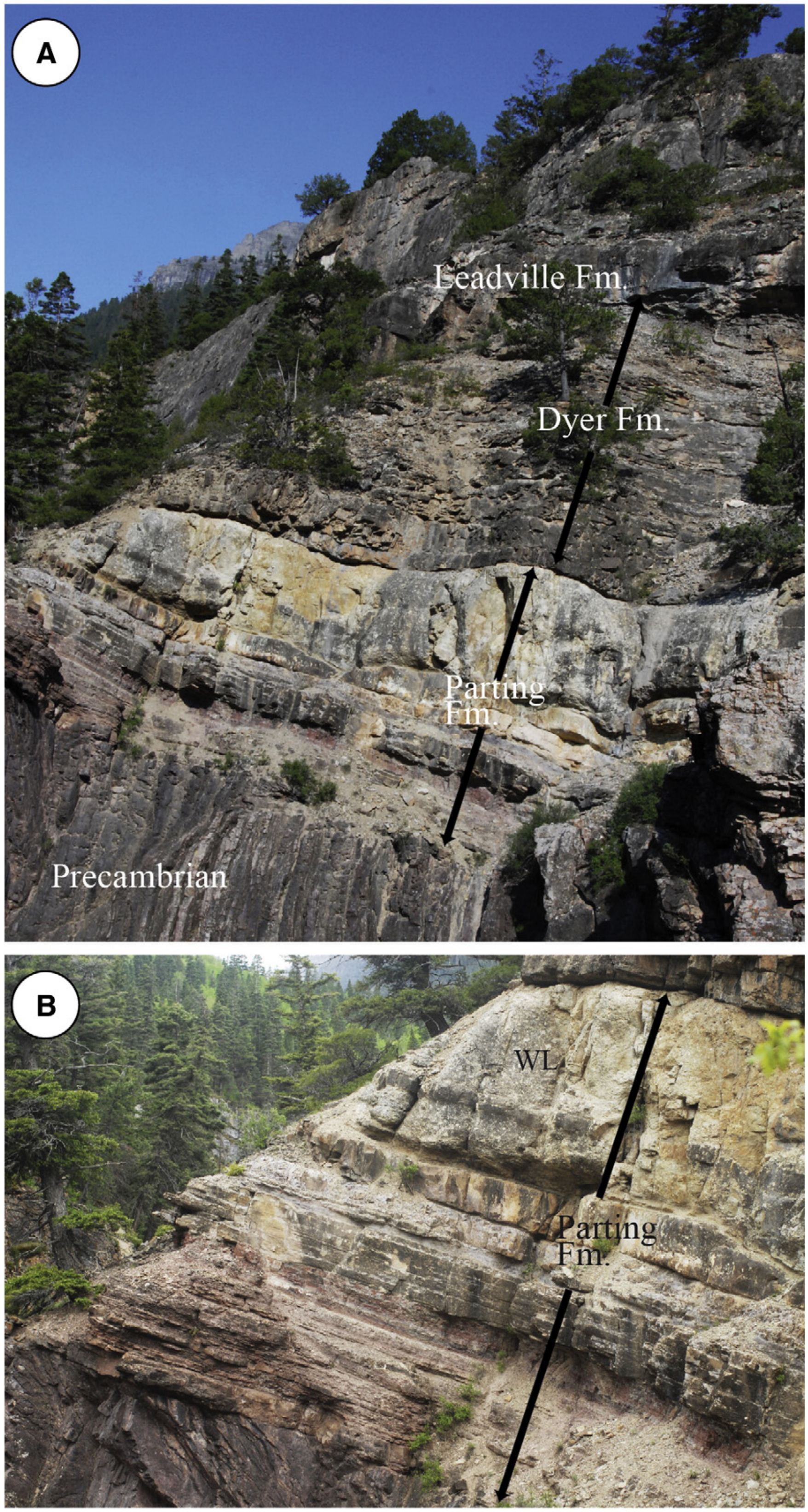

Fig. 3. Ouray, CO. (A) Devonian strata resting nonconformably on Precambrian basement. The Mississippian Leadville Limestone overlies the Parting and Dyer Formations of the Chaffee Group. (B) Close-up of Parting Formation (10.09 m thick) with red shale-rich facies at base, and white, massive limestone (WL) at the top. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

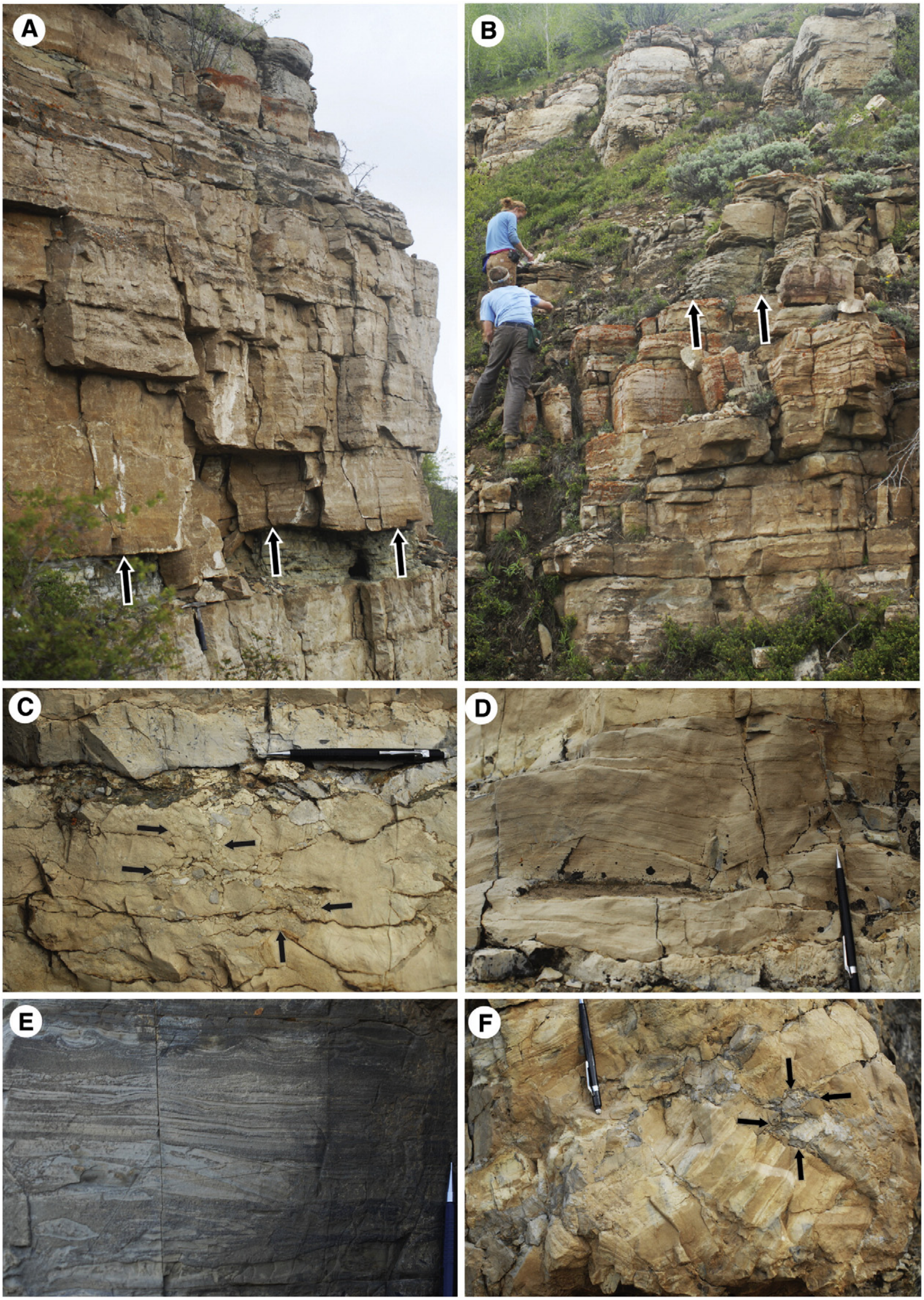

Fig. 4. Gilman, CO. (A) Poorly sorted granule conglomerate (3.95 m thick) of the Parting Formation (base shown by arrows). Hammer for scale. (B) Contact between the Parting and overlying Dyer Formation (arrowed). (C) Thin paleokarst breccia at 9.15 m with stained and corrugated upper surface, and dispersed fine to medium quartz sand grains. Arrows outline edges of filled dissolution cavities. (D) Laterally linked hemispheroid stromatolite bed at 9.35 m. (E) Bedding above 15.16 m with ripple cross-lamination, mudstone intraclasts, and soft-sediment deformation structures (at top). (F) Paleokarst breccia at contact between the Dyer and the overlying Mississippian Gilman Sandstone. Arrows outline edges of filled dissolution cavities. Photos C–F: pencil for scale is 14 cm long; tip is 2 cm long.

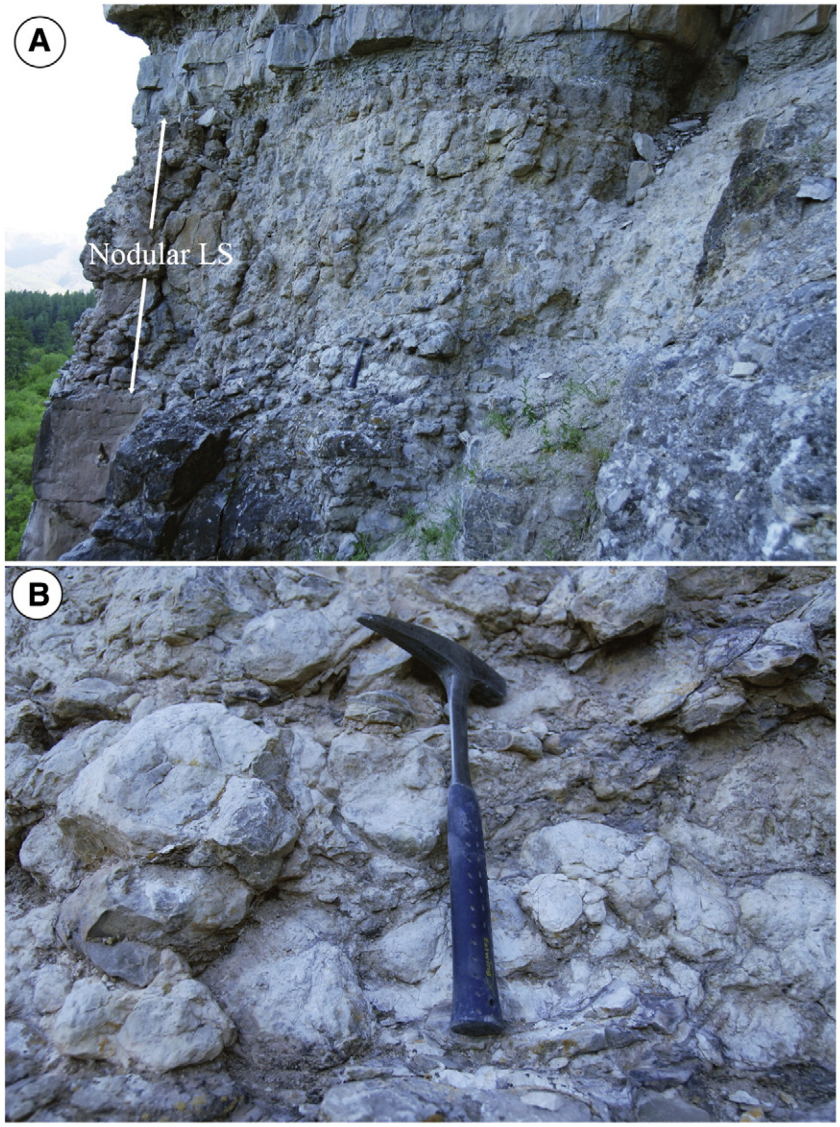

Fig. 5. Rockwood, CO. (A) Top of section with thick, limestone pseudoconglomerate. (B) Close-up of fabric of pseudoconglomerate. Hammer for scale in both photos.

a few paleokarst cavities with breccia and coarse sandstone (Fig. 4F), including some piped down from the overlying sandstone, which consists of well rounded, coarse-grained, quartz sandstone.

3.4. Dyer Formation: interpretation

At Cement Creek, the transition from trough cross-bedded sandstone at the top of the Parting Formation to bioturbated, fossiliferous wackestone indicates that the base of the Dyer Formation is a conspicuous regional flooding surface. The transition marks a shift from a transgressive sandy shoreline to an offshore marine carbonate setting. This transgression may have caused alluviation, a decreased local detrital influx, and deposition of pure carbonate. The fine grainstone and wackestone above are sharply overlain by the interval above 45.86 m that includes paleokarst breccia and overlying carbonate mudstone with karst pockets. The fitted fabrics and cement-filled cavities of the paleokarst breccia, and the karst pockets with small mudstone clasts and pink siltstone matrix reflect dissolution by meteoric waters, and later infilling by collapse and infiltration of eolian(?) silt. Lateral tracing of the overlying ~2 m thick interval above, which is capped by a 22 cm thick coarse sandstone, to a nearly 2 m thick bed of trough cross-bedded sandstone, suggest that a channel was cut and filled with sand at this level. Thus, the whole interval from 45.86 to 51.65 likely represents an interval of regressive events with a number of possible unconformities, the most significant of which may be marked by the channelized sandstone unit.

An interval at Glenwood Canyon, at almost the same stratigraphic position (48.68 m), also features a paleokarst of similar thickness, and an overlying mudstone bed with large cement-filled vugs (Myrow et al., 2011). Biostratigraphic data indicates that Middle *expansa* Zone conodonts exist below the paleokarst, but no conodont fauna have been recovered in the overlying Devonian strata up to the Mississippian unconformity (Sandberg and Poole, 1977; Sandberg and Dreesen, 1984; Myrow et al., 2011). Myrow et al. (2011) correlated a major positive carbon isotope excursion above the Glenwood Canyon paleokarst with the Hangenberg Event carbon isotope excursion, and noted that if correct, the upper Dyer Formation would be as young as the Middle to Late *praesulcata* conodont Zone, the uppermost conodont zone of the Famennian.

The unusual pseudobreccia at Rockwood Quarry in the upper part of the Dyer Formation, although somewhat different in character, is of similar thickness to that at Cement Creek and Glenwood Canyon. This similarity, combined with the facies transition above the pseudobreccia to fine-grained ribbon bedded carbonate, strongly supports a correlation to the same stratigraphic interval. In this case, however, instead of angular clasts of a paleokarst, the nodular fabric is typical of soil-forming textures. The paleokarst at Glenwood Canyon was interpreted as an unconformity produced by marine drawdown associated with the upper Famennian Hangenberg Event (Myrow et al., 2011). Thus, if the correlation to the Hangenberg excursion is correct, the recognition of paleokarst and paleosol beds of similar thickness and stratigraphic position at Cement Creek and Rockwood, respectively, suggest that the Hangenberg Event is manifested as a regionally developed unconformity, recording sea level fall across western Laurentia (Bless et al., 1993; Sandberg et al., 2002).

The ribbon-bedded carbonate mudstone and calcisiltite of the upper Dyer Formation at the Cement Creek and Rockwood sections are characteristic of low-energy marine facies deposited beyond wave- and tidal-influenced shorelines. These strata record the post-Hangenberg transgression, a global sea level rise (Dreesen et al., 1988; Isaacson et al., 1999, 2008; Kaiser et al., 2009). The meter-scale paleokarst cavities at the top of the Dyer reflect subaerial exposure associated with the regionally extensive Devonian–Mississippian boundary and deposition of the basal Gilman Sandstone Member of the Mississippian Leadville Limestone.

At Gilman, the abundance of paleokarst horizons in the Dyer, as well as the existence of possible gypsum pseudomorphs, indicate that this section of the Dyer was deposited in very shallow water. In this regard, the Gilman section appears to record relatively small-amplitude, high frequency changes in relative sea level, likely within a proximal setting. Given Gilman's location near the Homestake Shear zone, the area may have been topographically higher because of inherited structural relief due to Ordovician uplift along the fault system (Allen, 2004).

4. Stable isotope chemostratigraphy

4.1. Cement Creek

At Cement Creek, δ^{13}C values of the lower Parting Formation average ~ −1.5‰ (Fig. 6), with one small negative excursion down to ~ −3.5‰ at ~3 m, which is associated with the transition from grainstone to mudstone. Above 11.32 m, in the middle of the white marker bed in the upper Parting, values decrease to −4.20‰ at 13.97 m and remain around −4‰ up to the paleokarst at 16.25 m. δ^{13}C values in the overlying Broken Rib Member, above the paleokarst and sandstone of the upper Parting, trend positive from −2.31‰ (25.19 m) to an apex of 0.03‰ (37.43 m), then above a covered interval, drift negative to a nadir of −2.04 at 52.66 m. Above the paleokarst and sandstone deposits in the Coffee Pot Member, δ^{13}C values are enriched (0.57‰) and drift positive to a high of +5.63 at 63.38 m. Above this apex, δ^{13}C values decrease towards 2‰, with 2–3‰ oscillations superimposed on this general decline.

The δ^{18}O curve for the Parting Formation at Cement Creek increases slightly from −5‰ to −4‰, over which is superimposed a short negative δ^{18}O excursion at ~3 m that tracks the decrease in $\delta^{13}C_{carb}$ (Fig. 6). We observe no shift in $\delta^{18}O_{carb}$ across the Parting–Dyer contact and its associated paleokarst and sandstone intervals. A discontinuity in δ^{18}O values from −4 down to −11‰ occurs above a covered interval at ~32–36 m, which corresponds with the Broken Rib–Coffee Pot member boundary. The next ~5 m displays variability on the order of several per mil and a trend toward heavy δ^{18}O. Directly below the Hangenberg

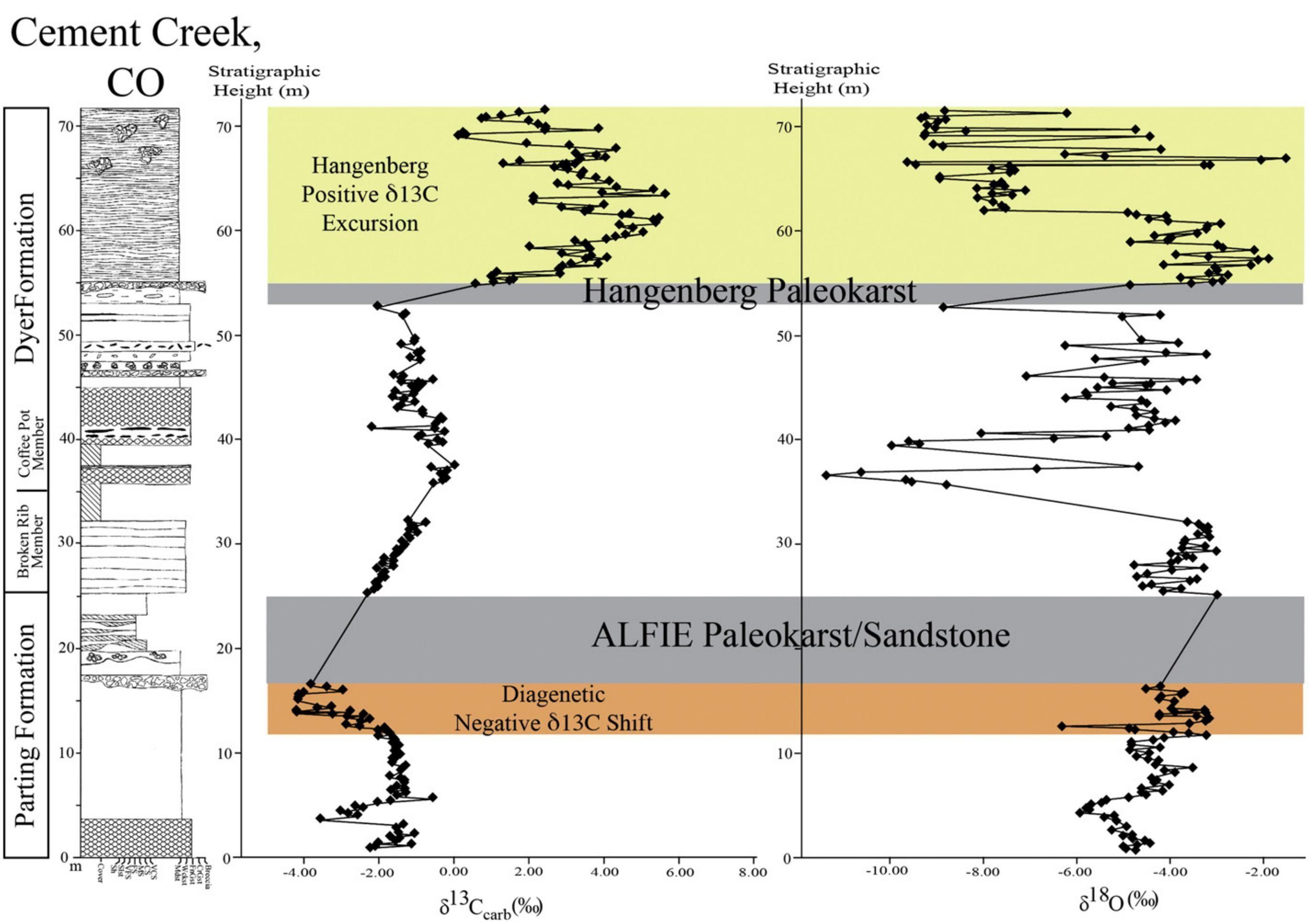

Fig. 6. Generalized stratigraphic column for Cement Creek, CO, and associated carbon and oxygen isotope curves. The position of the isotopic excursion ALFIE, at the Parting–Dyer Formation contact, and of the Hangenberg isotopic excursion, are shown in gray.

paleokarst (at 52.26 m), there is one $\delta^{18}O$ value of −8.86‰. Above the paleokarst, $\delta^{18}O$ values are more positive, although at ~63 m, $\delta^{18}O$ drops again to −8‰ for 3 m, and then becomes extremely variable towards the top of the section and the unconformity with Mississippian strata.

4.2. Ouray

The carbon and oxygen isotope data from Ouray covary, and for a short stratigraphic interval, display highly depleted oxygen and carbon isotopic values (Fig. 7). The Parting Formation (0–10.09 m) is generally characterized by a gradual decrease in both $\delta^{13}C$ and $\delta^{18}O$ values. $\delta^{13}C$ values initially oscillate between −4.24 and −5.52‰, and then drop to a nadir of −7.36‰. The $\delta^{18}O$ values begin at −4.93‰ and shift negative to values as low as ~−30‰ between 6.47 and 9.7 m. Both $\delta^{13}C$ and $\delta^{18}O$ values are much heavier above the Parting–Dyer formation contact. $\delta^{13}C$ values of the Dyer Formation average ~1‰, whereas $\delta^{18}O$ values range between −15.23 and −3.49‰.

4.3. Rockwood

Chemostratigraphic data from Rockwood, CO display covariance between carbon and oxygen isotope values (Fig. 8). $\delta^{13}C$ values at the base of the section are ~−1.8‰ and increase abruptly to −0.5‰ before gradually decreasing back to −2‰ at 3.73 m. Above this, values drop to as low as −6.84‰ at 4.49, then increase erratically back toward ~−4‰ and stabilize through 7.68 m. $\delta^{13}C$ values decrease between 7.91 and 9.46 m, reaching a nadir of −6.55‰ at 8.73 m. Values then rise slightly to −5.56‰ at 9.46 m. There are no data for the paleosol interval between 9.46 and 12.2 m, but above, $\delta^{13}C$ values resume at 0.36‰ and remain stable, varying between 1.41 and −0.24‰ until the top of the section.

$\delta^{18}O$ values at the base of the section are stable between 0.35 and 3.73 m, varying between −2.92 and −3.91‰ with a trend toward slightly more depleted values upsection (Fig. 8). Like the carbon data, values drop significantly above 4 m, and aside from a small increase between 5.13 and 5.96 m, the data generally drift negative below the paleosol. There is a small (~2‰) increase in $\delta^{18}O$ values above the paleokarst, although the $\delta^{18}O$ values do not approach the values at the base of the section. Data below the paleosol generally show covariance with the $\delta^{13}C$ data (Fig. 11) and there is insufficient isotopic variability above to assess further covariation.

4.4. Gilman

$\delta^{13}C$ data from Gilman initiate with an anomalously high value of 4.63‰ at 3.95 m (Fig. 9). From 4.17 to 10.88 m, values vary between −0.76 and 1.4‰, with a slightly decreasing trend upsection. At 10.88 m, $\delta^{13}C$ drops to as low as −2.85‰ at 11.44 m. Data are lacking from the paleokarst horizons between 11.7 and 14.19 m, but above, values are positive and trend from 0.22‰ to as high as 6.17‰. At 18.83 m, a large negative shift coincides with an interval dominated by paleokarst features. Above 20 m, $\delta^{13}C$ values begin a highly variable increase to 4‰ at ~23 m, at which point values stabilize somewhat and decrease slightly down to 2‰ at the top of the section.

$\delta^{18}O$ values at the base of the section (Fig. 9) are relatively invariant, and drift slightly negative below the paleokarst-rich interval above 11.7 m. Above the paleokarst, values are slightly higher, up to 18.83 m, at which point, the $\delta^{18}O$ values decrease to −22.02‰, in parallel with a decline in $\delta^{13}C$ values. Again, as with the carbon isotope

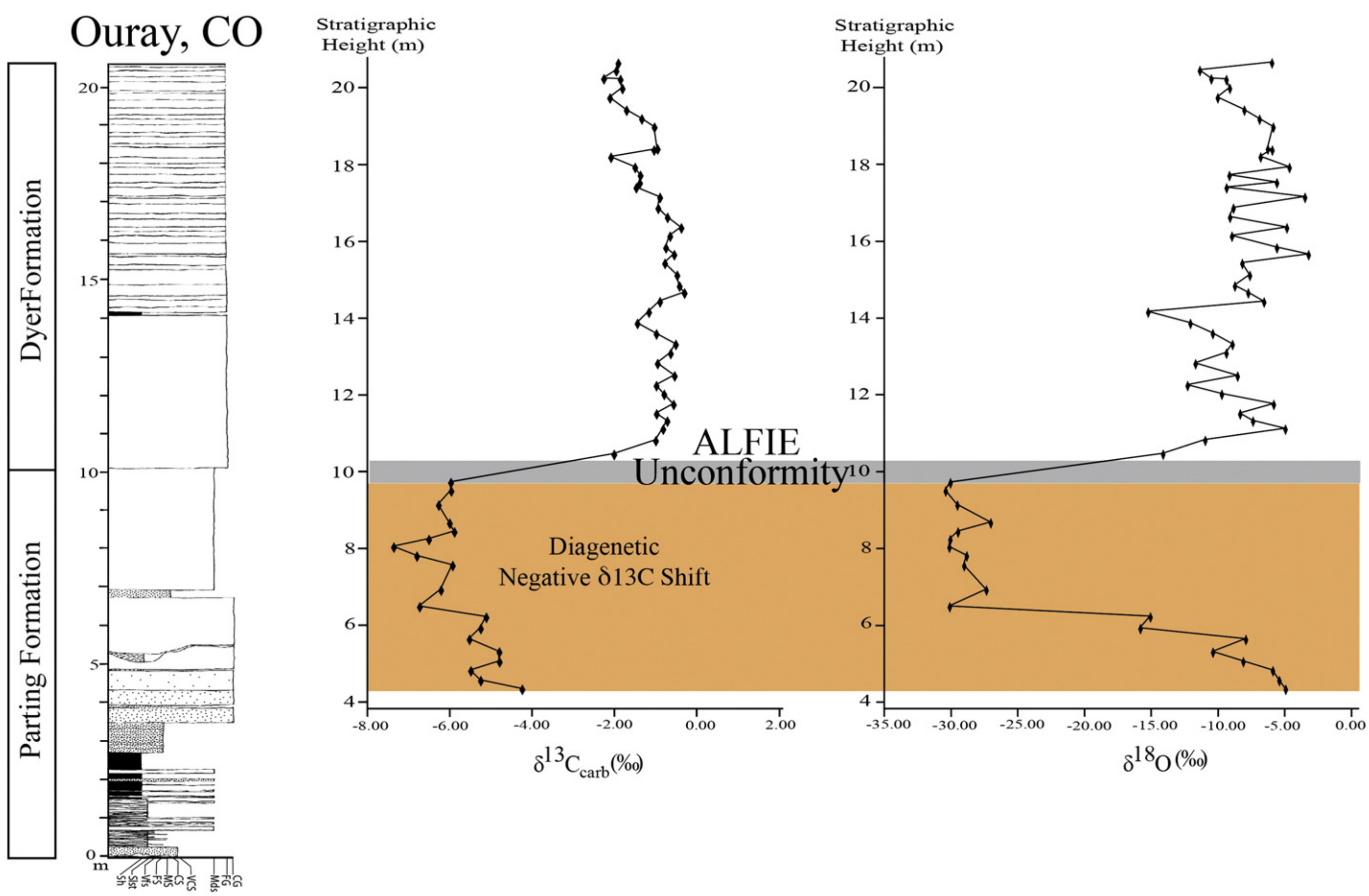

Fig. 7. Generalized stratigraphic column for Ouray, CO, and associated carbon and oxygen isotope curves. The position of the isotopic excursion ALFIE, at the Parting–Dyer Formation contact is shown in gray.

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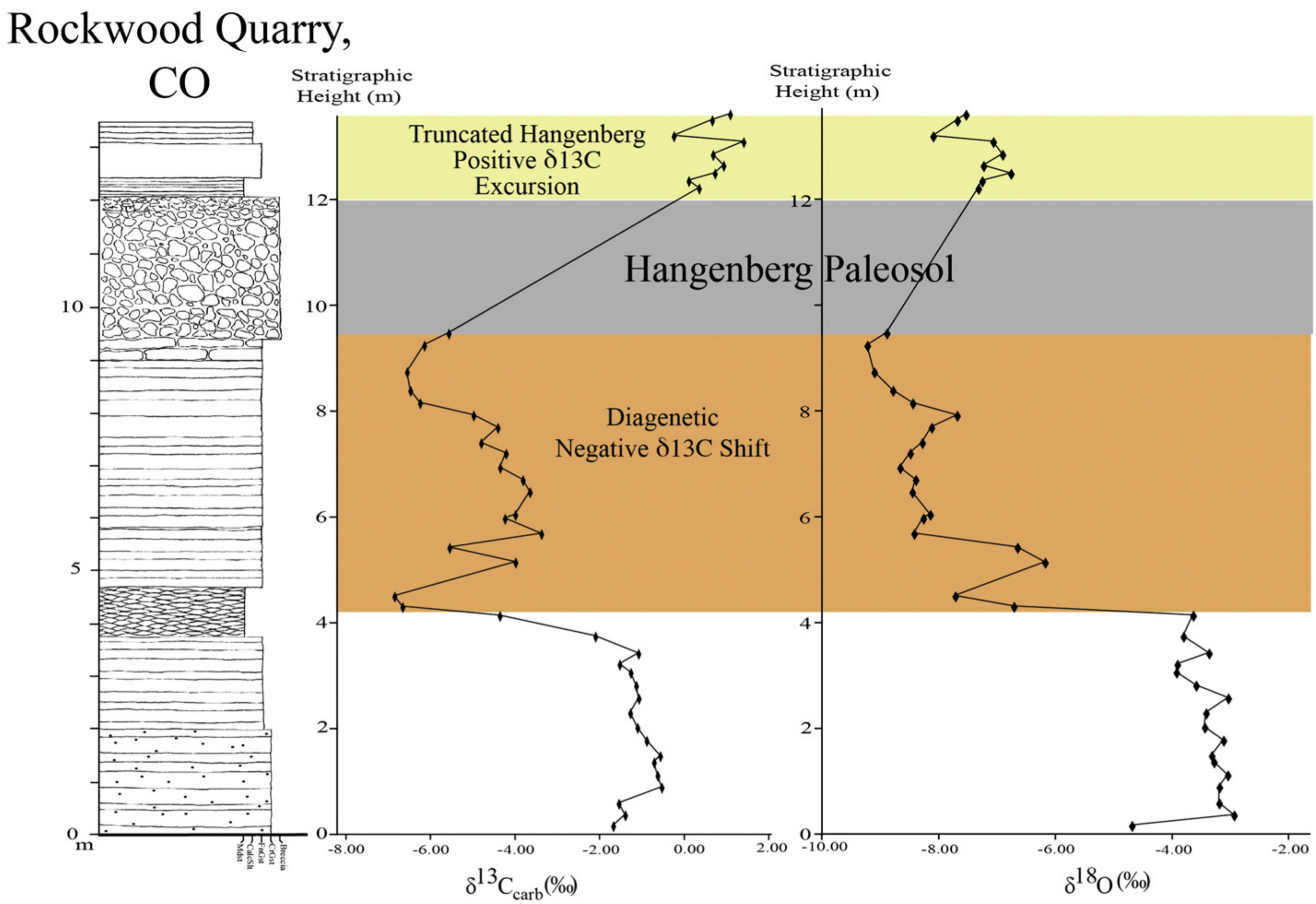

Fig. 8. Generalized stratigraphic column for Rockwood, CO, and associated carbon and oxygen isotope curves. The position of the Hangenberg Isotopic excursion is shown in gray.

data, values are low between 18.83 and 20.24 m, and then increase (with considerable scatter), from −17.73 to −2.23‰.

5. Interpretations

5.1. Parting–Dyer contact shift

Negative carbon isotope values at the base of the Parting Formation at Cement Creek (Fig. 6) match those of equivalent strata in Glenwood Canyon, Colorado (Fig. 10). Higher in the Parting, at both Cement Creek and Ouray, where carbonate lithologies dominate and allow for isotopic sampling, δ^{13}C values shift slightly negative below the unconformity at the Parting–Dyer contact. These negative δ^{13}C values below the formation boundary potentially signify diagenesis associated with exposure and alteration of underlying limestone with meteoric fluids. Unusual carbonate lithologies are interbedded with restricted marine lithofacies in the upper Parting at Glenwood Canyon. However, carbonate lithofacies within the Parting at Cement Creek have a typical marine character, and would thus be considered to contain a robust isotopic record of marine water at the time. The increase in δ^{13}C values across the formation boundary at Glenwood Canyon, Cement Creek, and Ouray sections, and the positive trending data in the lower Dyer Formation at Glenwood Canyon and Cement Creek, correlate well with two sections in Utah that record a Lower *expansa* Zone isotopic shift (ALFIE), tentatively correlated to the Dasberg Event (Fig. 10; Myrow et al., 2011).

At Ouray (Fig. 7), covariance in the oxygen and carbon isotopic data, both above and below the formation boundary, and the extremely negative δ^{18}O values, strongly support diagenetic alteration of a primary marine signal. Oddly, none of the other sections show such signal, and instead values are relatively similar below and above ALFIE.

5.2. Upper Dyer excursion

A large positive excursion, first detected in the Coffee Pot Member at Glenwood Canyon above a paleokarst interval, is correlated herein to several localities in central and western Colorado (Fig. 11). This positive excursion, combined with Middle *expansa* Zone conodonts in the Lower Coffee Pot (Sandberg and Poole, 1977) below the paleokarst, and a lower Mississippian age for overlying strata, led Myrow et al. (2011) to identify the isotopic shift as the Hangenberg carbon-isotope excursion (Buggisch and Joachimski, 2006; Cramer et al., 2008; Kaiser et al., 2008).

The δ^{13}C data from Cement Creek (Figs. 6, 11), and the thicknesses of stratigraphic units, closely matches the Glenwood Canyon section, aside from the lack of a large negative shift below the upper Dyer paleokarst. In particular, the enriched δ^{13}C values above the stratigraphically equivalent paleokarst intervals are nearly identical in architecture and magnitude. We correlate the paleosol in the upper Dyer Formation at Rockwood with the paleokarst horizons at Glenwood Canyon and Cement Creek. As with the Glenwood Canyon section, δ^{13}C and δ^{18}O values drift negative below the Rockwood paleosol (Fig. 11), and then jump to more positive values above. The short stratigraphic distance separating the paleosol from the overlying Devonian–Mississippian unconformity at Rockwood presumably resulted in stratigraphic truncation of the Hangenberg positive isotopic excursion.

We tentatively correlate the paleokarst interval from 11.7 to 14.19 m at Gilman, and the associated increase in isotope values above the paleokarst, to the Hangenberg Event. As with the Colorado sections, this positive shift is directly preceded by a negative shift in the carbon isotope data leading up to the paleokarst interval. The positive shift is abruptly truncated by a sharp negative shift in both

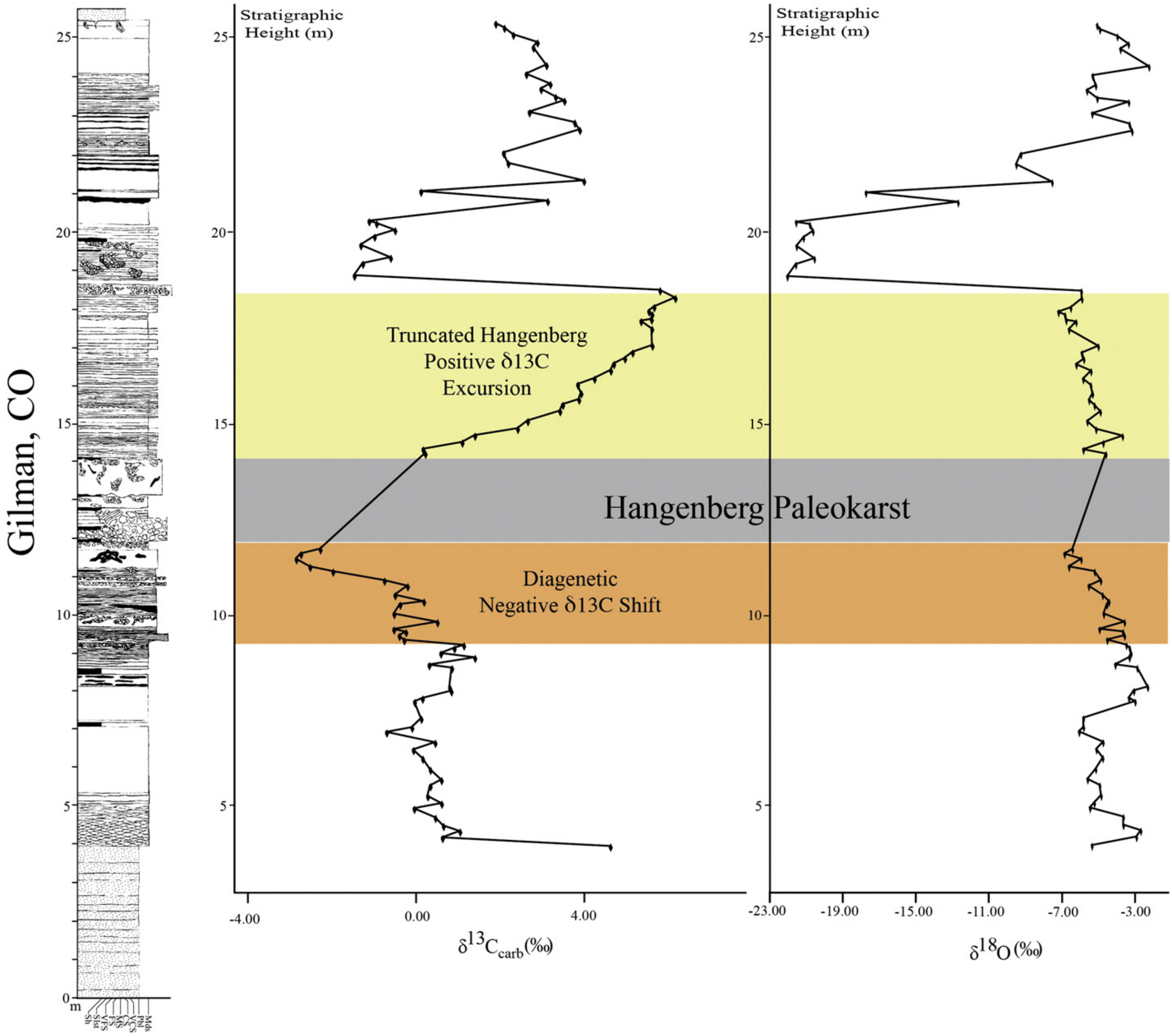

Fig. 9. Generalized stratigraphic column for Gilman, CO, and associated carbon and oxygen isotope curves. The position of the Hangenberg isotopic excursion is shown in gray.

carbon and oxygen isotopes at 18.83 m, corresponding with one of the many paleokarst horizons in the upper Dyer Formation at this site. We interpret this negative shift to represent truncation of the descending upper limb of the Hangenberg positive excursion. There are no biostratigraphic data to definitively constrain the positive shift with the upper Dyer (Hangenberg) excursion at other sections, as opposed to the Parting–Dyer isotopic shift (ALFIE), but the values are anomalously high and are thus consistent with the Hangenberg as observed in this study and globally.

6. Discussion

Published carbon isotope data exist for Upper Devonian strata (e.g., Buggisch and Joachimski, 2006), although most high-resolution data focus on the Frasnian/Famennian boundary interval (Stephens and Sumner, 2003; Goddéris and Joachimski, 2004; Buggisch and Joachimski, 2006). Data for the uppermost conodont zones (*postera*, *expansa*, and *praesulcata*) of the Famennian Stage, which include a record of the Dasberg and Hangenberg Events, show perturbations to the marine $^{87}Sr/^{86}Sr$, $\delta^{13}C$, and $\delta^{18}O$ values of seawater (Kürschner et al., 1993; Brand et al., 2004; Saltzman, 2005; Buggisch and Joachimski, 2006; Kaiser et al., 2006; Cramer et al., 2008).

Carbon isotopic data from Europe and Morocco for the Dasberg Event, which in sections lacking unconformities is approximately two-thirds of the way above the base of the Lower *expansa* Zone (Hartenfels and Becker, 2009), show positive values with little change across the event boundaries (Kaiser, 2005; Buggisch and Joachimski, 2006; Kaiser et al., 2008; Myrow et al., 2011). The carbon isotope shift in Lower *expansa* Zone strata of both Utah and Colorado (ALFIE) exceeds 3‰, and was tentatively correlated to the Dasberg Event (Myrow et al., 2011). Furthermore, Myrow et al. (2011) speculated about the presence of ALFIE in western U.S. sections and its apparent absence elsewhere (e.g., Europe and Morocco), specifically whether ALFIE is a regional or global phenomenon. They considered the following three possibilities:(1) western Laurentian water masses were partially isolated from the global ocean during part of the Early *expansa* Zone, and thus shifted to negative isotopic values due to local geochemical processes prior to the resumption of a global marine signature, recorded by the positive isotopic shift ALFIE (cf., Panchuk et al., 2006);(2) European and Moroccan sections did not record ALFIE due to a combination of stratigraphic

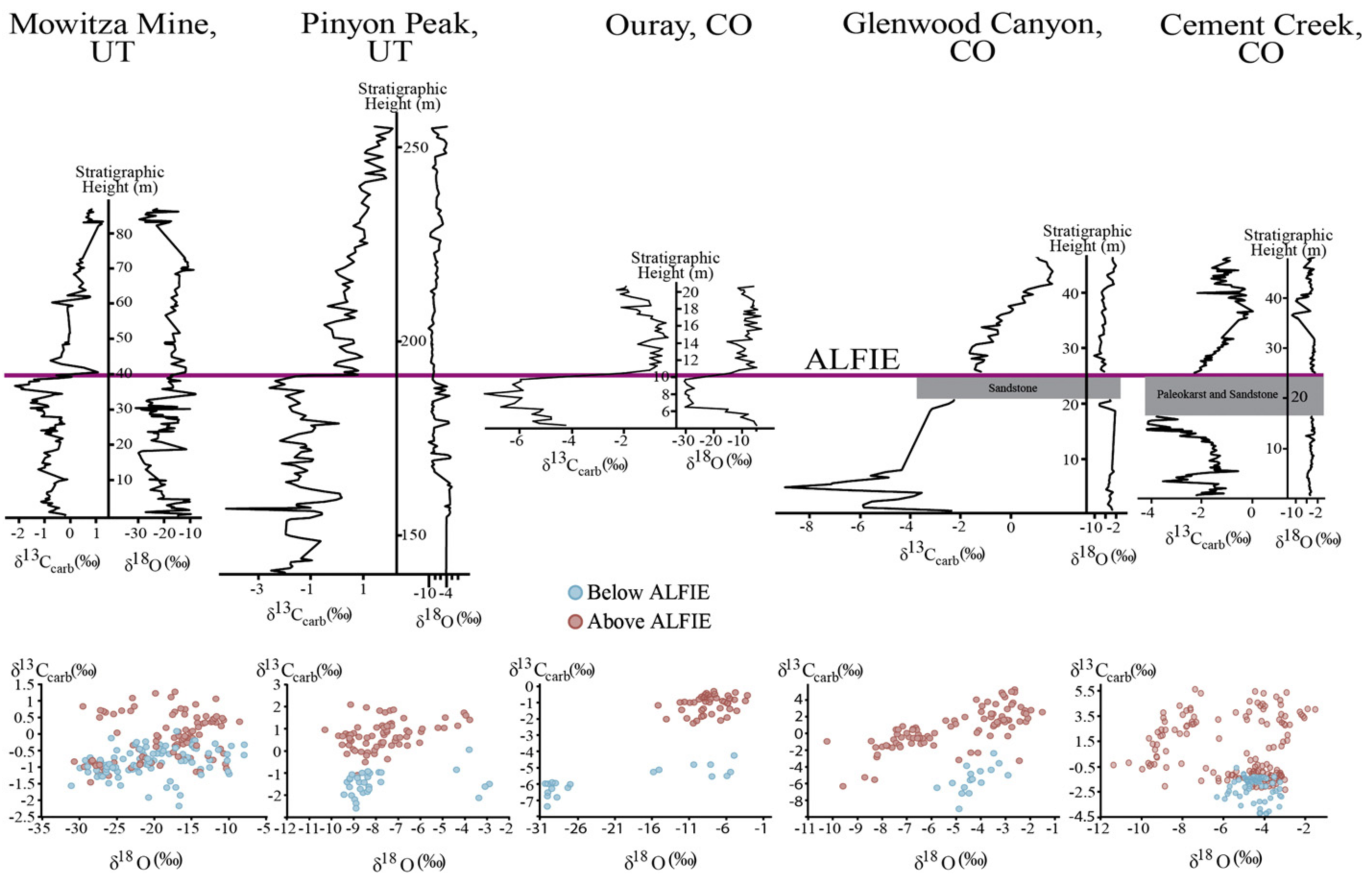

Fig. 10. Correlation of stratigraphic sections from Utah and Colorado, including the isotopic excursion ALFIE, which exists at the Parting–Dyer Formation contact in Colorado. The $\delta^{13}C$ and $\delta^{18}O$ data for these sections are provided, as well as cross-plots of $\delta^{13}C$ and $\delta^{18}O$, which distinguish between data below and above ALFIE.

condensation and a paucity of carbonate lithofacies in deep-water, siliciclastic-dominated successions; and (3) ALFIE reflects a diagenetic over-print of primary marine isotopic values.

The two sections in Utah that host ALFIE do not show any obvious sedimentological record of relative sea level change, or major lithofacies changes, across the isotopic shift (Myrow et al., 2011). These sections are distal relative to the more hinterland sections in Colorado. Carbon isotopic data for the Parting Formation at Glenwood Canyon, CO are sparse (Myrow et al., 2011) for lack of carbonate strata, and there is additional evidence for deposition in restricted and episodically hypersaline water masses in these strata (Myrow et al., 2011). Thus, we sought out hinterland Colorado sections that contain more abundant carbonate in Lower *expansa* Zone deposits of the Parting Formation, namely the Cement Creek and Ouray sections, to assess the regional extent and nature of ALFIE.

The sedimentological record of subaerial exposure and karstification at Cement Creek suggests that negative isotopic values present below the Parting–Dyer contact interval at various Colorado localities were produced through diagenetic reactions with meteoric fluids. This is particularly important, given the spatially discontinuous nature of the paleokarst interval, and thus the potential for missing evidence of lowstand. The shapes of the $\delta^{13}C$ and $\delta^{18}O$ curves are highly variable (Fig. 10), as is the degree of covariance. At Ouray, where neither a paleokarst nor a transgressive sandstone unit is present at the top of the Parting, the extraordinarily negative oxygen isotopic values (> -30‰) provide strong support for a diagenetic origin of ALFIE at this site. $\delta^{13}C$ data for Cement Creek show a similar shift to negative values below the Parting–Dyer contact, but also record a much thicker section of Parting carbonate, the lower part of which (below ~10 m) shows values similar to those directly above in the lower Dyer.

The significant differences between the paired isotopic curves for these sections, and the variation in the shape of the $\delta^{18}O$ and $\delta^{13}C$ curves for all the sections that contain ALFIE, including the Utah sections (Fig. 10), is consistent with variable diagenetic alteration below an unconformity surface in Colorado, and either a cryptic unconformity or correlative conformity in Utah. Such alterations likely involved fluid–fluid and fluid–rock interactions that transformed originally aragonitic minerals to calcite (Allan and Matthews, 1982; Derry, 2010), and possible incorporation of ^{12}C-enriched CO_2, derived from remineralization (Knauth and Kennedy, 2009) or thermal alteration (Derry, 2010) of organic matter, into synsedimentary authigenic carbonate, thereby altering primary $\delta^{13}C$ values. If so, changing paleobathymetry in the western U.S., as recorded in the different parts of the Devonian western seaway, would have resulted in alteration below exposure surfaces. The signal in sections proximal to the Rocky Mountains appears to record a limited depth of alteration (~5–10 m; Ouray and Cement Creek) below obvious exposure surfaces. Oddly, alteration below much more cryptic surfaces in the Pinyon Peak and Mowitza Mine sections within the Sevier foreland of Utah, show negative $\delta^{13}C$ values for thick sections (many tens of meters), although the accumulation rates for any of our sections are unknown. Even more surprisingly, $\delta^{18}O$ values commonly show little change below ALFIE, except for the Ouray section. Both the Mowitza Mine and Ouray sections show extremely depleted $\delta^{18}O$ values below ALFIE, yet at the former site the overlying strata are not very enriched either, which suggests that the oxygen isotopes at the site record wholesale alteration. In any case, if the relative sea level fall documented for this interval in Colorado is coincident with the Dasberg Event (Myrow et al., 2011), then it is possible that it was driven by eustasy, so that during the Dasberg Event alteration of exposed shallow marine strata by meteoric water took place across western North America (cf.,

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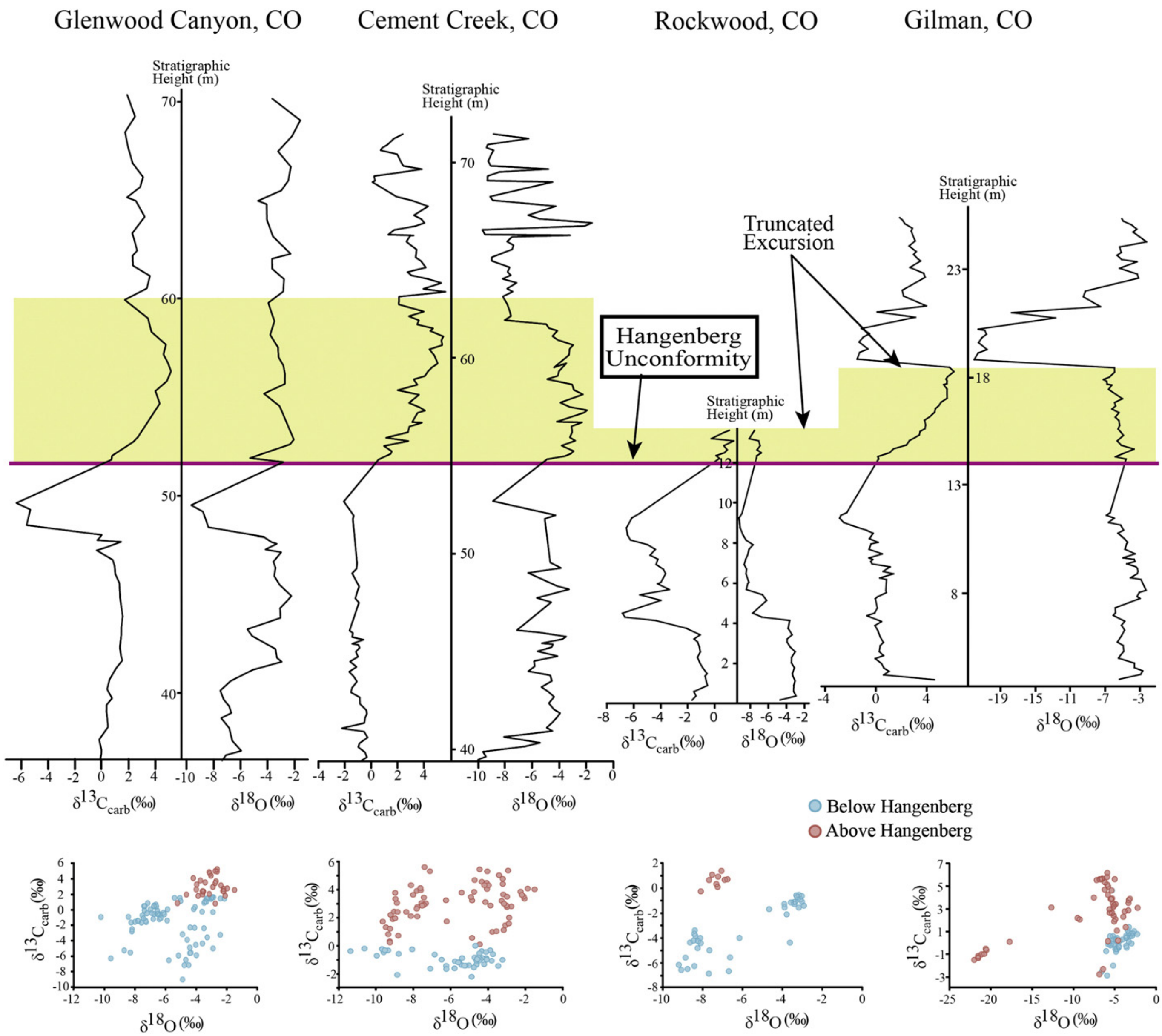

Fig. 11. Correlation of stratigraphic sections from Utah and Colorado, including the Hangenberg isotopic excursion, which exists at the Parting–Dyer Formation contact in Colorado. The $\delta^{13}C$ and $\delta^{18}O$ data for these sections are provided, as well as cross-plots of $\delta^{13}C$ and $\delta^{18}O$, which distinguish between data below and above the Hangenberg Event.

Knauth and Kennedy, 2009). At some localities, alteration could have taken place within meteoric water lenses (Hathaway et al., 1979; Knauth and Kennedy, 2009), regardless of whether the site was subaerially exposed.

The paleokarst and positive carbon isotopic shift in the upper Dyer Formation is correlated to the Hangenberg Event (Myrow et al., 2011). Our study demonstrates that both the paleokarst and associated positive isotopic anomaly are widespread across central and western Colorado, although detailed regional mapping of the paleokarst has not been done to show whether it is continuous or discontinuous in nature. In this region of North America, regression caused widespread karstification and diagenetic alteration of exposed carbonate, the latter of which produced negative $\delta^{13}C$ values, most likely associated with meteoric waters charged with remineralized terrestrial organic matter (e.g., Allan and Matthews, 1982; Swart and Kennedy, 2012). The very high $\delta^{13}C$ values in the overlying strata record the Hangenberg secular isotopic rise associated with transgression and the resumption of carbonate deposition (Brand et al., 2004; Saltzman, 2005; Buggisch and Joachimski, 2006; Kaiser et al., 2006; Cramer et al., 2008; Kaiser et al., 2008). The pattern of depleted carbonate in the regressive deposits and enriched carbonate in the transgressive strata is consistent with $\delta^{13}C$ patterns in <10 Ma carbonate shelf deposits, which reflect eustatic controls on the distribution of enriched $\delta^{13}C$ aragonitic sediment (Swart, 2008).

Results provided herein show that regionally extensive $\delta^{13}C$ chemostratigraphic changes may result from meteoric diagenetic alteration associated with relative (and possibly eustatic) sea level lowstands. The sedimentological signatures of lowstand range from well exposed paleokarst intervals (Cement Creek, Rockwood Quarry, CO), to sharp lithological changes with no paleokarst (Glenwood Canyon, CO), to carbonate-to-carbonate transitions but with bleached and recrystallized limestone below (Ouray, CO), to apparently conformable contacts with no evidence of differential alteration (Pinyon Peak and Mowitza Mine, UT). The latter case is particularly instructive, given the assumption in most studies that regionally correlative isotopic variations represent global secular changes in ocean chemistry. In detail, our data show that a highly variable degree of diagenetic depletion of $\delta^{13}C$, and even greater variability in $\delta^{18}O$, took place below the two lowstand surfaces during late Devonian events in western Laurentia.

Such variability, where present in other data sets, is commonly interpreted as a record of primary spatial heterogeneities in the water column at the time of deposition (e.g., Panchuk et al., 2006). Thus, the results of this study suggest caution in the interpretation of spatially variable, isochronous isotopic data. Our findings, which center on strata with biostratigraphic age control, are also potentially instructive with regard to debates concerning the origin of widespread $\delta^{13}C$ anomalies in Precambrian strata, an interval with relatively poor temporal constraints beyond the application of carbon isotope chemostratigraphy (Knauth and Kennedy, 2009; Derry, 2010; Grotzinger et al., 2011; Swart and Kennedy, 2012).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.palaeo.2013.05.021.

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