Carbon isotope stratigraphy and correlation of plant megafossil localities in the Hell Creek Formation of eastern Montana, USA

Nan Crystal Arens*
Department of Geoscience, Hobart & William Smith Colleges, Geneva, New York 14456, USA

A. Hope Jahren
Department of Geology and Geophysics, University of Hawai‘i, Honolulu, Hawai‘i 96822, USA

David C. Kendrick
Department of Geoscience, Hobart & William Smith Colleges, Geneva, New York 14456, USA

ABSTRACT

Questions of biotic and environmental change during deposition of the Upper Maastrichtian Hell Creek Formation require a robust and replicable system for intraformational correlation of fossil localities. In this paper, we present a carbon isotope chemostratigraphic curve based on terrestrial organic carbon. Data were taken from a complete measured section spanning the full 93 m of the Hell Creek Formation at our study site. Sedimentary beds were described at the centimeter scale, and samples for carbon isotope analysis were taken at ~10 cm intervals. Each sedimentary bed was analyzed in thin section, and grain-size data were assembled based on petrographic point counts. The well-documented Cretaceous-Paleogene boundary negative carbon isotope excursion, six negative carbon isotope excursions, and four tentative positive carbon isotope excursions provide chronostratigraphic tie points within the Hell Creek Formation. We used this curve to precisely correlate 12 additional fossil-bearing localities from throughout the Hell Creek Formation across its type area. These correlations revealed significant local variation in sediment accumulation rates, confirming that simple stratigraphic position relative to the diachronous base and top of the Hell Creek Formation introduces significant error in correlation.

*arens@hws.edu

INTRODUCTION

Initial paleobiological research in the Hell Creek Formation (Upper Maastrichtian, Upper Cretaceous) focused on collecting its rich dinosaur fauna, a task that did not require a detailed time-stratigraphic framework (Clemens and Hartman, this volume). In the last two decades of the twentieth century, research shifted to patterns of diversity, extinction, and survivorship across the Cretaceous-Paleogene boundary, which could be diagnosed by the geochemical and mineralogical signature of the terminal Cretaceous impact (e.g., an iridium- and shocked mineral-bearing boundary clay; Smit and Hertogen, 1980; Orth et al., 1981; Bohor et al., 1984; Libekmo et al., 1987) and by distinctive floral and faunal assemblages (Archibald et al., 1987; Nichols, 1990, 2002; Nichols and Johnson, 2002; Woodburne, 2004; Bercovici et al., 2009). The detailed exploration of biotic change across the Cretaceous-Paleogene boundary led to new questions of climatic, environmental, floral, and faunal change during Hell Creek time (e.g., Johnson and Hickey, 1990; Johnson, 2002; Wilf et al., 2003; Wilson, 2005). However, such questions require a robust and detailed time-stratigraphic framework that permits intraformational correlation of fossil localities across a wide geographic area. Such correlation can be challenging in terrestrial environments where deposition is generally episodic and local, and where rates and styles of sedimentation can vary significantly over relatively short distances.

Various approaches to intraformational correlation have been discussed or applied. The simplest of these marks the stratigraphic distance between fossil localities and formational contacts. While practical in the field and a good approximation locally, this approach can provide only rough correlation if sedimentation rates vary across a region or if stratigraphic contacts are time transgressive. Some (e.g., Frye, 1969; Moore, 1976) have suggested a scheme of lithostratigraphic members within the Hell Creek Formation that might aid correlation. However, an examination of stratigraphic sections across a wider region shows that this variation is not laterally consistent and therefore not useful for correlation (Murphy et al., 2002). Magnetostratigraphy offers greater time-stratigraphic precision, but it provides only a single point of correlation within the Hell Creek Formation: the C30n-C29r transition. This magnetic reversal has been recognized between 24.5 m and 10.5 m below the Hell Creek–Fort Union formational contact (Archibald, 1982; Swisher et al., 1993; Hicks et al., 2002), illustrating significant variation in sedimentation rate across the basin. The base of C30n has not been recognized in the Hell Creek Formation; C29r ends in the Paleocene, after Hell Creek time. Radioisotopic age dating has not provided useful correlations within the Hell Creek Formation. Volcanic ash has been successfully dated in the Fort Union Formation (Swisher et al., 1993). In the Hell Creek Formation, only three well-preserved ash layers have been identified in North Dakota (Hicks et al., 2002); none has thus far yielded precise dates (Hicks et al., 1999), and none is laterally continuous over distances that would make it useful for intraformational correlation. In eastern Montana, little unworked volcanic material has been preserved within the Hell Creek Formation. Biostratigraphy provides additional data. Lancian and Puercan mammal faunas bracket the Cretaceous-Paleogene boundary in eastern Montana, allowing this faunal transition to be recognized (Woodburne, 1977, 2004; Archibald et al., 1987), although some traditionally Puercan elements have recently been shown to have first appearance in latest Cretaceous sediments (Archibald et al., 2011). However, despite some faunal change during Hell Creek time (Wilson, 2005), there are as yet no comparable biostratigraphic subdivisions for mammals within the late Maastrichtian. Similarly, palynostratigraphy allows easy recognition of the Cretaceous-Paleogene boundary (e.g., Nichols, 1990, 2002; Bercovici et al., 2009), but, to date, geographic rather than temporal variation appears to dominate the Maastrichtian pollen and spore record (Nichols and Sweet, 1993). Johnson and Hickey (1990; see Johnson [2002] for discussion and an updated interpretation) recognized stratigraphic zonation in plant megafossils. As with mammals and palynomorphs, the most significant megafossil transition occurred at the Cretaceous-Paleogene boundary. However, Johnson and Hickey (1990) recognized a second floral transition (between the HCI and HCII megafossil zones) 15–21 m below the Hell Creek–Fort Union formational contact (see Johnson [2002] for the revised stratigraphic positions indicated here) that appeared to be correlated to climate change (Wilf et al., 2003). A third transition (between HCI and HCII megafossil zones) at ~50 m below the Hell Creek–Fort Union formational contact (Johnson and Hickey, 1990) was marked by the last appearance of eight leaf morphotypes, with many of the most common forms ranging through (Johnson, 2002). This led Johnson (2002) to conclude that although the lower Hell Creek flora (HCI megafossil zone) was distinct, the HCI-HCII zone boundary is not biostratigraphically useful. Moreover, this megafossil biostratigraphy has not yet been tested outside of Johnson’s southwestern North Dakota field area.

Between 1999 and 2008, our team collected material from ~30 plant megafossil localities within the Hell Creek type area in Garfield and McCone Counties, Montana (see Arens and Allen, this volume). Approximately half of these occurred within the Hell Creek Formation. In many cases, neither the top nor the bottom of the formation was visible from the locality, and the relative stratigraphic position of these collections was uncertain. Because the relative stratigraphic position of localities is essential to questions of change through time, we sought a way to better constrain the relative stratigraphic position of these localities. Toward this goal, we began to explore carbon isotope chemostratigraphy using land plant substrates (Arens and Jahren, 2000, 2002; Arens et al., 2000; Jahren et al., 2001, 2008; Jahren and Arens, 2009) as an additional tool that could be added to the repertoire of approaches discussed earlier.

Carbon isotope chemostratigraphy has been extensively applied in marine rocks (e.g., Kah et al., 1999; Brenchley et al., 2003; Wang et al., 2007; Beauchamp et al., 2009; Takashima et al., 2009). Terrestrial rocks were not initially sampled for
Carbon isotope chemostratigraphy because researchers assumed that the carbon isotopic signal of atmospheric CO₂ in terrestrial substrates was masked by organisinal vital effects. However, Koch et al. (1992) demonstrated that carbon isotope values of mammalian tooth enamel could be used to correlate between marine and terrestrial records at the Paleocene-Eocene boundary, which is marked by a negative carbon isotope excursion in marine rocks (Kennett and Stott, 1991; Dickens et al., 1995; Magioncalda et al., 2004; Domingo et al., 2009). Since the carbon isotope signature of mammalian herbivores comes directly from their plant food, Arens et al. (2000) proposed C₁₅N of lignite beds cannot be correlated except by physically tracing them at outcrop scale. This conclusion has been verified by radioisotopic data demonstrating distinct ages for basal Fort Union Formation lignites across the region (Swisher et al., 1993).

The Hell Creek Formation is characterized by regularly bedded, variegated siderite-bearing siltstone interbedded with very fine- to fine-grained sandstones, mudstone, carbonaceous shale and rare lignite (Fastovsky and Dott, 1986; Fastovsky, 1987; Murphy et al., 2002). Unlike southwestern North Dakota (Murphy et al., 2002), there is no evidence of marine sedimentation within the Hell Creek Formation of eastern Montana. Paleosol development is common in Hell Creek Formation siltstones and spans a continuum of soil development from Entisols to Inceptisols to Alfisols (Fastovsky and McSweeney, 1987; Retallack, 1994), depending on the degree of soil development that occurred before the soil surface was buried by a subsequent depositional event. Entisols show very weak soil development, with root traces, persistent primary sedimentary structures, and a lack of soil structure development (Retallack, 1994). Inceptisols represent an intermediate grade of soil development in which most primary sedimentary structures have been obliterated, and clay has begun to accumulate in subsurface horizons. Alfisols, base-rich well-drained soils, are characterized by the migration of clays into the subsurface, the development of horizon structure, and clay-skinned slickensides (Retallack, 1994). In Garfield County, the Hell Creek Formation was deposited between ca. 67.7 Ma and 65.58 Ma, representing an estimated 2.1 m.y. (Wilson, 2005).

GEOLOGIC SETTING

The Hell Creek Formation was first described from the drainage of Hell Creek (Garfield County) in eastern Montana (Brown, 1907). Brown failed to designate a formal stratotype section, which would logically have served as a reference section for chemostratigraphic correlation. Reported thickness of the formation varies from ~170 m at an unspecified locality in the region (Thom and Dobbins, 1924) to ~114 m at the mouth of Hell Creek. Rigby and Rigby (1990) concluded that the formation thickens to the west and south. Based on a similar fossil fauna (Triceratops zone) and flora, the Hell Creek Formation from the Wiliston Basin was correlated with the Late Cretaceous–Early Eocene Fox Hills Formation of the Powder River Basin (Brown, 1914). Within its type area, the Hell Creek Formation overlies the orange-yellow sandstones and mudstones of the Fox Hills Formation and locally the bright white sandstone of the Colgate Member of the Fox Hills Formation (Hartman, 2002). The Hell Creek Formation underlies the Fort Union Formation. In the Hell Creek type area, the base of the Fort Union is represented by the Tullock Member (Hartman, 2002), which is characterized by lignite beds that are laterally persistent at the outcrop scale, and variegated mudstones (Fastovsky and Dott, 1986; Fastovsky, 1987). At the outcrop scale, lignite beds represent very local deposition within a stratigraphic zone at the base of the member in which lignite accumulation was favored (Collier and Knechtel, 1939). Therefore, individual lignite beds cannot be correlated except by physically tracing them at outcrop scale. This conclusion has been verified by radioisotopic data demonstrating distinct ages for basal Fort Union Formation lignites across the region (Swisher et al., 1993).

The location of the Hell Creek Formation carbon isotope reference section at Herman Ridge (Fig. 1; Appendix 1) was chosen to be a continuous exposure including both the lower contact with the Fox Hills Formation (Colgate Member at this site) and the upper contact with the Fort Union Formation. It contained few covered, slumped, or deeply weathered intervals and had reasonable access. The site is close to the Fort Peck Reservoir and to the west of most fossil localities, in terrain with very steep slopes where erosion has produced abundant, minimally weathered exposures.

The Herman Ridge section was trenched to fresh surface using hand tools and measured in July and August 2002. Bed contacts were identified, and bed thickness was measured to the nearest centimeter using a laser level, Jacob staff, and hand tape. The color, lithology, sedimentary structures, and fossil content of each bed were described, and samples were taken for carbon isotope and grain-size distribution analysis. Sediment samples for carbon isotope composition were collected at ~10 cm intervals, except in lenticular sandstones, which tend to be organic poor and thus were sampled by unit, and in paleosols, where only the upper portion of the paleosol (O-horizon if possible) was sampled in order to minimize alteration of the isotopic signature by within-soil metabolic processes. We did sample within two
paleosols (samples MT02-174 to MT02-177 and MT02-173 to MT02-169; Appendix DR1) to assess this variation.

Identifying the Base of the Hell Creek Formation

At the location of the Herman Ridge section (Fig. 1), the Fox Hills Formation is 11.3 m thick and displays a sharp and undulating contact with the underlying Bearpaw Shale. The Fox Hills Formation is beige to orange, moderately well sorted, very fine-grained sandstone. Grains are well rounded, and both feldspar and mafic mineral grains were visible in hand sample. Sandstone was grain supported with interstitial fines. Beige beds were friable; orange beds were well cemented with a color-bearing mineral. Fox Hills beds ranged from 10 cm to 1 m in thickness and varied from structureless to cross-bedded. Symmetrical ripples and interference ripples were observed on some bedding planes. Cone-in-cone structures were preserved in zones 3–8 cm thick and overlain by structureless sand beds ranging from 30 to 50 cm thick. Some sand beds were draped by clay interbeds, which were up to 5 mm thick. In the upper ~4 m of the Fox Hills Formation, laterally continuous shale interbeds developed. Shale beds ranged from 10 to 40 cm thick and showed plane-parallel lamination. Interbedded sands were cross laminated, and the contacts between sand and shale were irregular.

Figure 1. Location of the plant megafossil and stratigraphic reference section localities within Garfield and McCone Counties, Montana.

GSA Data Repository Item 2014026—Carbon isotope data, weight percent organic carbon data, petrographic point count data, and rock type categories observed in samples from Herman Ridge and numerous fossil-bearing sections—is available at www.geosociety.org/pubs/ft2014.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.
The Colgate Member of the Fox Hills Formation overlies the beige-orange portion of the Fox Hills Formation at the reference section locality. Here, the Colgate Member is 6.2 m thick and very light gray at the base, grading into bright white up section. At this locality, the Colgate Member forms a bright white band in outcrop that is distinct at distance. Colgate sand was very fine grained, well rounded, and moderately well sorted. In this location, the unit was well cemented. Grains were predominantly quartz, with few mafic mineral grains, very rare feldspar grains, and no lithic grains. The unit was structureless at the base of the Herman Ridge section, although cross-beds were visible locally. The lower contact with the beige-orange Fox Hills Formation was erosional. The contact with the overlying Hell Creek Formation was sharp, erosional, and undulating, with up to 2 m of local relief. These incised channels were partially filled with a lag that was up to 10 cm thick and included iron-oxide concretions, plant fragments, charcoal, rare bone, clay rip-up clasts, and pebbles. We placed the lower contact of the Hell Creek Formation at this erosional surface.

**Identifying the Top of the Hell Creek Formation**

In the type area, the top of the Hell Creek Formation is generally placed at the base of the first lignite bed that can be traced at the outcrop scale (Brown, 1938; Fastovsky, 1987). However, the nature of this basal Fort Union lignite is regionally variable. At the Hell Creek Road locality (Arens and Jahren, 2000), this lignite (historically referred to as the Z-coal) was ~1.6 m thick and represented continuous lignite deposition with only thin (<20 cm) partings of carbonaceous shale, siltstone, and volcanic ash. In contrast, at locations such as Hauso Flats (Swisher et al., 1993; Arens and Jahren, 2000; the locality is referred to as Hauso Flat in the latter reference) and the area around Brownie Butte (Fastovsky, 1987; see also Helen’s Leaves and Rick’s Place, discussed below), lignite beds that mark the formational contact were separated by up to 2 m of carbonaceous shale and mudstone, and some of these lignites were not laterally traceable for more than a few hundred meters. To accommodate this variation, Fastovsky (1987) proposed a series of criteria to distinguish the Hell Creek–Fort Union formational contact. In addition to the base of the lowest laterally continuous lignite, the Hell Creek–Fort Union formational contact can be recognized as the top of the highest swelling claystone and the base of the lowest occurrence of variegated facies (Archibald, 1982; Fastovsky, 1987). Murphy et al. (2002) further suggested placing the contact at the color change from the grayish tones of the Hell Creek Formation to beige or yellow tones typical of the Fort Union Formation. We place the Hell Creek–Fort Union formational contact at the base of the lowest lignite that could be traced laterally at outcrop scale that was above the highest swelling clay and below the lowest variegated beds. Most lignites that defined the Hell Creek–Fort Union formational contact were significantly less than 1 m in thickness.

**Grain-Size Distributions**

A single rock sample for grain-size analysis was taken from each distinct bed. Rock samples were embedded with epoxy to prevent crumbling of friable lithologies during thin sectioning. Grain-size ratios were calculated from 192 point counts made on gridded petrographic thin sections. At each point, the composition of the slide was classified as sand, silt, or clay (based on grain size), or organic matter (based on color). Pore space was not counted; cement was a negligible component of these rocks.

**Carbon Isotopic Analyses**

For bulk organic carbon isotope measurements, a 1–5 g sample of rock from the Herman Ridge section was crushed and acidified in 1 M HCl overnight to remove carbonate. A standard weight sample of the remaining residue was analyzed for δ13C value in triplicate. Samples were analyzed for δ13C value using a Eurovector automated combustion system in conjunction with an Isoprime stable isotope mass spectrometer. Samples were introduced to the combustion system in pure tin capsules. All carbon isotope values are reported in the standard δ13C notation (δ = [(Rsample − Rstandard)/Rstandard] × 1000‰) with reference to the Pee Dee belemnite (PDB) limestone standard (Rstandard = −1.106‰). Uncertainty in each carbon isotope measurement associated with mass spectrometry is ±0.05‰. Weight percent organic carbon content of sediment samples was calculated from these data. Carbon isotope analyses on samples from the Herman Ridge section were completed in 2003–2004. Sediment samples from fossil localities were collected and analyzed over several years from 1997 to 2000. We followed the same preparation and analytical protocol with these samples but, in some cases, used a different mass spectrometer. Every carbon isotope value reported represents the mean of three replicate analyses. For samples analyzed after 2000, the standard deviation of these analyses is reported in Appendix DR1 (see footnote 1). For carbon isotope values produced before 2000, only standard deviations greater than 0.05‰ were reported. We note that 2000 marked the move of A.H. Jahren’s isotope laboratory from Georgia Institute of Technology to the Johns Hopkins University, which accounts for the shift in reporting protocol.

During review of this manuscript, work by Larson and colleagues (2008) came to our attention. They noted that the common diagenetic carbonate mineral siderite (FeCO3) has a lower solubility compared to calcite and speculated that it might not be completely removed from sediment during acidification with 1 M HCl. Larson et al. (2008) were specifically concerned about in situ and fumigation acidification techniques in which aqueous acid is added to sample-bearing combustion capsules prior to insertion into an automated sampler, and sediment cores are exposed to acid vapor, respectively. As a solution, Larson et al. (2008) proposed in situ treatment with 6 M HCl, which they concluded eliminated siderite from samples. The in situ method also retained soluble organic compounds...
important to accurate C:N measurements, a priority for their method (Larson et al., 2008).

In the Hell Creek Formation, siderite is ubiquitous as concretions, as a coating on sand grains, as cement in sandstones, and as a skin of paleosol structures and slickensides. In sampling, we avoided concretions and well-cemented or orange-colored sandstones. We further sampled the interior of soil structures rather than areas coated by diagenetic minerals. Therefore, high concentrations of siderite were avoided by our standard field sampling procedures. With geological samples such as ours, little soluble organic matter is preserved, so conserving soluble organic compounds is not a priority as with Larson et al. (2008). We removed reactive carbon-bearing secondary minerals by soaking finely ground samples in acid, as described already. The acid was then decanted, and the remaining residue was washed three times in deionized water prior to isotope analysis. Our previous work has found this sufficient to remove iron-oxide minerals associated with modern soils (Werts and Jahren, 2007). The decant method allows us to use abundant acid to react all of the carbonate minerals present. A full analysis of the effect of siderite on carbon isotopic values of the Hell Creek Formation samples is beyond the scope of this paper, and funds were not available for re-preparation and reanalysis of our samples. However, we assessed the behavior of siderite in our sample preparation protocol (Appendix 2) and concluded that 93% of siderite was removed by our protocol. Given small starting masses of siderite in the Hell Creek Formation samples and the relatively low mass of carbon in siderite, any residual inorganic carbon would contribute very little to the resulting carbon isotopic values. Therefore, our carbon isotopic values are unlikely to be strongly biased by residual inorganic carbon. However, a thorough investigation of our preparation technique is an important avenue for future research, and we note that samples with low organic carbon content, of which there are many in Hell Creek Formation sediments, may be particularly vulnerable to even a small amount of siderite contamination.

Data reduction, statistical analysis, and visualization were performed in Microsoft Excel 11.1.1 and Aabel 1.5.8.9 for Macintosh.

Taphonomic Considerations

The choice of bulk sedimentary organic carbon as a substrate for carbon isotope analysis is based on the observation that the carbon isotopic compositions of plants and their atmosphere are correlated and that this correlation is strongest when several varieties of co-occurring C₃ plants are sampled and averaged (Lloyd and Farquhar, 1994; Arens et al., 2000). In moist climates, this sampling regime effectively minimizes variation due to physiological and ecological vital effects (Arens et al., 2000), which can be problematic when individual plants or other biomolecules are measured. In the sedimentary environment, organic material on terrestrial floodplains will come mostly from plants and will mix a variety of co-occurring species, thus accomplishing the goal of a mixed sample (Arens and Jahren, 2000). In our early work, we sampled both bulk sedimentary organic carbon and a mixed assemblage plant cuticle isolated from individual sediment samples (Arens and Jahren, 2000, 2002; Jahren et al., 2001). This approach separated the vascular land plant signal from any microbial signal. In all cases, the carbon isotope values of mixed samples of isolated plant cuticle and bulk sedimentary organic carbon were strongly correlated (Arens and Jahren, 2000, 2002), showing that this labor-intensive method did not produce a more faithful record of secular variation in land plant carbon isotope values than did bulk sedimentary organic carbon alone. In addition, we have shown that δ¹³C values of sedimentary organic carbon were not correlated with sedimentary facies or rock type (Arens and Jahren, 2000, 2002). We have further shown that the ability to accurately reconstruct the carbon isotopic composition of atmospheric CO₂ using terrestrial sedimentary organic carbon is not compromised by incursion of marine water in estuarine systems (Jahren and Arens, 2009). This might be of concern in the lowermost portions of the section, where sedimentological evidence hints at tidal influence within an estuary (Flight, 2004; Arens and Allen, this volume).

Principles of Chemostratigraphic Correlation

C₃ land plants sample CO₂ from the well-mixed atmosphere during photosynthesis and discriminate between the stable isotopes of carbon in a known way during carbon fixation (Farquhar et al., 1989). The isotope composition of plant tissue thus reflects the composition of the atmosphere under which it was fixed (Medina et al., 1986; Van der Merwe and Medina, 1989; Jahren et al., 2008), with a quantifiable error of ~1‰ due to physiological vital effects (Arens et al., 2000), although greater isotopic discrimination has been observed in arid climates (Ehleringer, 1989; Feng and Epstein, 1995). Therefore, secular variation observed in the carbon isotope signature of a mixed sample of terrestrial plants that grew under mesic conditions generally represents carbon isotopic variation in paleoatmospheric CO₂ (Arens and Jahren, 2000; Arens et al., 2000; Carvajal-Ortiz et al., 2009), although extreme local conditions may override a signal from the well-mixed atmosphere in unusual cases (e.g., Tabor et al., 2007). Although employing different carbon-bearing substrates, this method has been used extensively to correlate marine (e.g., Kah et al., 1999; Myrow et al., 2002; Tewari and Sial, 2007; Wang et al., 2007; Zhu et al., 2007; Morrow et al., 2009; Takashima et al., 2009; Ainsaar et al., 2010; Hück et al., 2010) and terrestrial (Arens and Jahren, 2000, 2002; Retallack et al., 2005; Carvajal-Ortiz et al., 2009; Yans et al., 2010) sediments. Since there is seldom an objective way to distinguish one carbon isotope excursion from another, chemostratigraphy is best applied in conjunction with other chronostratigraphic tools, such as biostratigraphy, magnetostratigraphy, sequence stratigraphy, and radios isotopic dating (e.g., Brenchley et al., 2003; Beauchamp et al., 2009; Morrow et al., 2009; Ainsaar et al., 2010). The correlations we propose in this study are made within the known stratigraphic
context of each section, as discussed next. Carbon isotope stratigraphy is used primarily to refine correlations.

In developing a chemostratigraphic correlation, we sought to identify features of the carbon isotope curve that can be matched among sections (Arens and Jahren, 2002). (1) Excursions are reversible anomalies that are above or below the average signal. Excursions may encompass one or more stratigraphic samples, and the most extreme values of the excursion must fall outside of the 95% confidence interval of the five-point running average of the stratigraphic section surrounding the excursion. A notable example of an excursion is the −1.5‰ to −2.0‰ carbon isotope anomaly in surface-ocean dissolved inorganic carbon in the centimeters above the Cretaceous-Paleogene impact layer at the global stratotype section at El Kef, Tunisia (Keller and Lindinger, 1989; Keller et al., 1996). This excursion has been well studied and identified in other marine sections (e.g., Hsü et al., 1982; Perch-Nielsen et al., 1982; Smit, 1982; Zachos and Arthur, 1986; Stott and Kennett, 1989; Zachos et al., 1989, 1992; Robin et al., 1991; D’Hondt et al., 1998). The Cretaceous-Paleogene excursion has also been documented in land plant tissue and sedimentary organic carbon in terrestrial sections (e.g., Arens and Jahren, 2000, 2002; Gardner and Golmou, 2002), which demonstrates the link between the marine and terrestrial carbon reservoirs via the atmosphere and land plant photosynthesis. (2) Cycles, which may be of uniform or variable duration, are repeating quasiperiodic components of an average signal and may represent orbitally forced variation in carbon cycling. (3) Shifts are abrupt (<200 k.y.) deviations from the average signal that persist for a number of samples. Shifts may be reversible, but they differ from excursions, in which recovery to pre-excursion values generally occurs over a short stratigraphic distance (<1 m). In contrast, shifts represent values that persist over many samples and stratigraphic distance greater than 1 m. (4) Trends are directional changes in isotope composition through time. Finally, (5) the absolute value of excursion or shift maxima and the magnitude of excursions and shifts may be useful for establishing boundary conditions and distinguishing among excursions and shifts (Arens and Jahren, 2002).

RESULTS

Carbon isotope values for organic carbon, percent organic carbon, and grain-size data are presented in Appendix DR1 (see footnote 1).

Taphonomic Analyses

In the Herman Ridge section, we confirmed previous results (Arens and Jahren, 2000, 2002) showing that percent sedimentary organic carbon calculated from mass spectrometer results was uncorrelated with carbon isotope value (N = 386, R = 0.03, p = 0.59). A similar result was obtained when carbon isotope value was regressed on percent organic carbon as calculated from petrographic point counts (N = 99, R = 0.08, p = 0.41). Not surprisingly, the percent of organic matter calculated from mass spectrometer data was well correlated with the same measure calculated from petrographic thin sections (N = 99, R = 0.44, p << 0.001). Therefore, we conclude that carbon isotope values were not systematically biased by the amount of organic matter preserved. Therefore, siderite contamination appears not to have produced consistently high carbon isotope values in low-organic-carbon samples.

To assess the relationship between rock types and carbon isotope values, each carbon isotope measurement from the Herman Ridge section was coded with its associated rock type based on field observations (carbonaceous shale, lignite, claystone/mudstone, sandstone, siltstone, and paleosol; Appendix DR1). Descriptive statistics for the carbon isotope values of these groups are presented in Table 1. We performed pairwise comparisons of these rock-type categories using the nonparametric Mann-Whitney test because lignite and paleosol samples failed the homogeneity of variance requirement for parametric methods. The Mann-Whitney test assesses the difference between the distributions of two independent samples. Carbonaceous shale (N = 4) offered too few samples for accurate calculation of p-values and will not be considered further. At α = 0.01, we failed to reject the null hypothesis that carbon isotope values from lignite, claystone/mudstone, siltstone and paleosol were sampled from the same underlying population. This result is surprising because soil scientists have recognized that within-soil carbon cycling alters the carbon isotopic composition of soil organic material (Nissenbaum and Schallinger, 1974; Melillo et al., 1989; Balesdent and Mariotti, 1996; Anundson et al., 1998; Ehleringer et al., 2000). While we noted within-soil variation of 0.7‰ in the two paleosols that we sampled internally, this variation is not significant and does not appear to bias the utility of paleosol samples for carbon isotope chemostratigraphy. In contrast, the population of sandstone samples differed from all but the lignite samples at the same level of significance. However, the average

<table>
<thead>
<tr>
<th>TABLE 1. DESCRIPTIVE STATISTICS OF CARBON ISOTOPE VALUES FROM THE HERMAN RIDGE SECTION GROUPED BY ROCK TYPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonaceous shale</td>
</tr>
<tr>
<td>Sample size</td>
</tr>
<tr>
<td>Mean</td>
</tr>
<tr>
<td>Median</td>
</tr>
<tr>
<td>Standard deviation</td>
</tr>
<tr>
<td>Variance</td>
</tr>
</tbody>
</table>
carbon isotope value for the population of sandstone samples ($\delta^{13}C = -24.59\%$) was second lowest only to carbonaceous shale (Table 1), suggesting that siderite contamination, which would generate higher values, did not produce the observed difference. However, this result contradicts that of our earlier analysis in which carbon isotope values from all rock types were derived from the same underlying population (Arens and Jahren, 2000).

Figure 2. Bulk organic carbon isotope data from 99 sediment samples taken through the Hell Creek Formation carbon isotope reference section plotted against (A) the percent of sand and (B) silt present in each sample based on point-count analyses. A modest ($R = 0.22$) but statistically significant ($p = 0.03$) negative correlation was observed for sand. A modest ($R = 0.23$) but statistically significant ($p = 0.02$) positive correlation was observed for silt.

Figure 2. Bulk organic carbon isotope data from 99 sediment samples taken through the Hell Creek Formation carbon isotope reference section plotted against (A) the percent of sand and (B) silt present in each sample based on point-count analyses. A modest ($R = 0.22$) but statistically significant ($p = 0.03$) negative correlation was observed for sand. A modest ($R = 0.23$) but statistically significant ($p = 0.02$) positive correlation was observed for silt.

Sedimentary grain-size ratio data (Appendix DR1) allow rock-type relationships to be tested with continuous, rather than categorical, data. Carbon isotope composition of bulk sedimentary organic carbon was uncorrelated with the percent clay in a sample ($N = 99$, $R = 0.07$, $p = 0.50$). However, carbon isotope values were negatively correlated with the proportion of sand ($N = 99$, $R = 0.22$, $p = 0.03$; Fig. 2) and positively correlated with the proportion of silt ($N = 99$, $R = 0.23$, $p = 0.02$; Fig. 2). Although these correlations were not particularly strong, we hypothesized that some sort of carbon winnowing mechanism might explain this result. To test this, we regressed the proportion of organic carbon in each sample as calculated from mass spectrometer data onto the proportions of sand, silt, and clay. We predicted that sand-rich samples would be poor in organic carbon, thus explaining the negative correlation. The proportion of sand in a sample was uncorrelated with its proportion of organic carbon ($N = 99$, $R = 0.10$, $p = 0.30$). A similar result was obtained for clay ($N = 99$, $R = 0.07$, $p = 0.50$). However, the proportion of silt in a sample was negatively correlated with percent organic carbon ($N = 99$, $R = 0.22$, $p = 0.03$), suggesting that some winnowing of organic carbon might have influenced this size fraction.

To the extent that the measured proportion of organic carbon, rock type as described in the field, and grain-size ratios derived from petrographic thin sections represent differences in depositional and preservation environment, these results suggest that carbon isotope values for these terrestrial sediments are not strongly dependent on facies. However, the results reported for sandstones bear further investigation.

Features of the Herman Ridge Section Useful for Chemostratigraphic Correlation

The carbon isotope curve for the Herman Ridge section (Fig. 3; Appendix DR1 [see footnote 1]) yielded a number of features that are potentially useful for intraformational correlation. Using the criteria described previously, we identified seven negative (including the Cretaceous-Paleogene boundary excursion) and tentatively identified four positive carbon isotope excursions within the Hell Creek Formation (Table 2). We noted that all of these features occurred in mudstone or siltstone samples, suggesting that they are unbiased by distributional variations associated with sandstone. However, the positive excursions generally occurred in samples with very low organic carbon content, which would be most vulnerable to even a small amount of contamination by residual inorganic carbonate. This observation leads to the provisional interpretation of the positive carbon isotope excursions. Although they are noted on the section, they are not used as primary evidence for correlation. Further study of these features is needed.

We identified the Cretaceous-Paleogene boundary carbon isotope excursion by its stratigraphic position near (~0.87 m) the Hell Creek–Fort Union formational contact and by its absolute value and relative magnitude ($\Delta\delta^{13}C$, which is the difference between the minimum value of the excursion and the value
The minimum value of the proposed Cretaceous-Paleogene carbon isotope excursion at the Herman Ridge section (δ¹³C = −26.47‰; Table 2) was similar to those reported at Cretaceous-Paleogene boundary sections in which the boundary had been diagnosed by the presence of an iridium-and shocked mineral–bearing boundary clay (Arens and Jahren, 2000). At these sections, δ¹³C values range from −26.08‰ to −26.28‰ in the centimeters above the Cretaceous-Paleogene boundary iridium anomaly. The excursion in the Herman Ridge section was also of similar magnitude (Δδ¹³C = −2.03‰; Table 2) to those reported at confirmed Cretaceous-Paleogene boundaries, where Δδ¹³C values range from −1.5‰ to −2.8‰ (Arens and Jahren, 2000). Carbon isotope values immediately below the Cretaceous-Paleogene horizon in this section (δ¹³C = −24.26‰; Appendix DR1 [see footnote 1]) were also similar to those reported at confirmed Cretaceous-Paleogene boundary sections (δ¹³C values range from −24.26‰ to −24.92‰; Arens and Jahren, 2000). While we do not currently have biostratigraphic evidence to bracket the Cretaceous-Paleogene boundary at this site, the stratigraphic position of this excursion and its magnitude make it a good candidate for correlation with confirmed Cretaceous-Paleogene boundary excursions in this region.

We also recognized a negative excursion (Neg1 in Fig. 3; Table 2) ~2.5 m below the Cretaceous-Paleogene excursion. The Neg1 excursion can be distinguished from the Cretaceous-Paleogene boundary excursion by its lower absolute value and magnitude (Table 2). We noted an excursion similar to Neg1 in published marine data from Kjølby Gaard section in Denmark (Kaminski and Malmgren, 1989), which supports our interpretation that it represents a global signal and is thus useful for regional correlation.

Like the Cretaceous-Paleogene boundary excursion and Neg1, negative excursions Neg2, Neg4, and Neg5 (Fig. 3; Table 2) were each expressed in a single sample (Appendix DR1 [see footnote 1]). In contrast, Neg3 (Table 2) was spread over four samples (Appendix DR1) and had two discrete negative peaks (Fig. DR1 [see footnote 1]). Neg6 consisted of two values outside of the 95% confidence interval for the five-point running average carbon isotope values (Appendix DR1). In contrast, positive carbon isotope excursions Pos2 and Pos3 were distributed over three samples each, Pos4 over two samples, and only Pos1 was represented by a single sample (Appendix DR1).
Some cyclic variation was also suggested at the base of the formation. Beginning at the Fox Hills–Hell Creek formational contact, values trended negative to a low point punctuated by the Neg6 excursion (Fig. 3). Values then trended positive to a high point punctuated by the Pos4 excursion. Carbon isotope values trended negative again to the Neg5 excursion, trended positive to the Pos2 excursion, and trended negative again to the Neg4 excursion. We recognized no shifts or directional trends in this section.

CORRELATION OF PLANT MEGAFOSSIL LOCALITIES WITHIN THE HELL CREEK FORMATION

The goal of this work was to seriate fossil localities within the Hell Creek Formation. We begin with the correlation of five localities (Fig. 4) from the central Hell Creek type area (Fig. 1) that represent the upper portion of the formation. These were arguably the most straightforward correlations because they can be physically linked to the Hell Creek–Fort Union formational contact and, in some cases, the Cretaceous-Paleogene boundary iridium and shocked mineral anomaly. All data are provided in Appendix DR1 (see footnote 1).

Mushroom Butte

The Mushroom Butte locality (Fig. 1; Appendix 1) is within sight of the Hauso Flats locality (Fig. 1, UCMP PB 99058) where an iridium- and shocked mineral–bearing boundary clay (Smit and van der Kaars, 1984; Swisher et al., 1993) and the −2.5‰ carbon isotope excursion (Arens and Jahren, 2000) mark the Cretaceous-Paleogene boundary. The lignite layer at Hauso Flats and the associated boundary claystone can be traced laterally to the equivalent layer—a carbonaceous shale—at Mushroom Butte, allowing us to place the Cretaceous-Paleogene boundary with precision at Mushroom Butte (Fig. 4). As expected, the −2.1‰ Cretaceous-Paleogene boundary carbon isotope excursion appears within the same carbonaceous shale layer at Mushroom Butte as was observed at Hauso Flats (Arens and Jahren, 2000). Furthermore, the minimum value of the proposed Cretaceous-Paleogene boundary excursion at Mushroom Butte (−26.21‰; Appendix DR1) is close to that observed in the same bed at Hauso Flats (−26.08‰; Arens and Jahren, 2000). The similarity of both absolute value and magnitude of these excursions supports the proposed correlation. Plant megafossils at Mushroom Butte occur in Hell Creek Formation sediments and were deposited prior to the terminal Cretaceous impact. Thus, they represent a latest Cretaceous flora on a well-drained substrate.

Figure 4 further shows that the Cretaceous-Paleogene boundary at Mushroom Butte appears ~2 m above the Hell Creek–Fort Union formational contact, as recognized by the lowermost lignite above swelling claystone and below the lowest occurrence of variegated facies (Archibald, 1982; Fastovsky, 1987). At Mushroom Butte, the lowermost lignite is modest, only ~8 cm thick and rich in siliciclastic sediment. The contact at Mushroom Butte contrasts with that at Hauso Flats, where the Ir-bearing lignite is also the lowest lignite above swelling claystone (Smit and van der Kaars, 1984; Swisher et al., 1993). Thus, at Hauso Flats, the Cretaceous-Paleogene boundary and the formational contact coincide. The difference in the placement of the Cretaceous-Paleogene boundary (a chronostratigraphic marker) and the formational contact (an environmental marker) at Mushroom Butte may be explained by local topographic variation that permitted the initiation of lignite deposition at Mushroom Butte prior to that at other nearby locations.

TABLE 2. STRATIGRAPHIC POSITION AND ABSOLUTE VALUES OF CARBON ISOTOPE EXCURSIONS RECOGNIZED IN THE HERMAN RIDGE SECTION

<table>
<thead>
<tr>
<th>Excursion</th>
<th>Stratigraphic position relative to Khc-PgFtu contact (m)</th>
<th>δ¹³C value (%)</th>
<th>Magnitude (%)</th>
<th>Standard error (p-value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-Pg</td>
<td>−0.87</td>
<td>−26.47</td>
<td>−2.03 (−2.21)</td>
<td>0.32 (p &lt; 0.01)</td>
</tr>
<tr>
<td>Neg1</td>
<td>−3.60</td>
<td>−25.64</td>
<td>−1.31 (−1.80)</td>
<td>0.21 (p &lt; 0.01)</td>
</tr>
<tr>
<td>Neg2</td>
<td>−36.29</td>
<td>−26.35</td>
<td>−1.74 (−1.95)</td>
<td>0.38 (p &lt; 0.01)</td>
</tr>
<tr>
<td>Neg3</td>
<td>−56.80 to −57.26</td>
<td>−26.59</td>
<td>−2.14 (−2.49)</td>
<td>0.81 (p &lt; 0.01)</td>
</tr>
<tr>
<td>Neg4</td>
<td>−65.45</td>
<td>−27.06</td>
<td>−2.73 (−2.66)</td>
<td>0.13 (p &lt; 0.01)</td>
</tr>
<tr>
<td>Neg5</td>
<td>−74.12</td>
<td>−25.58</td>
<td>−1.61 (−1.50)</td>
<td>0.13 (p &lt; 0.01)</td>
</tr>
<tr>
<td>Neg6</td>
<td>−82.16 to −82.36</td>
<td>−27.57</td>
<td>−3.09 (−4.28)</td>
<td>0.70 (p = 0.02)</td>
</tr>
<tr>
<td>Pos1</td>
<td>−38.98</td>
<td>−21.15</td>
<td>+2.25 (+2.60)</td>
<td>0.28 (p &lt; 0.01)</td>
</tr>
<tr>
<td>Pos2</td>
<td>−69.56 to −69.96</td>
<td>−21.27</td>
<td>+1.79 (+1.68)</td>
<td>0.15 (p &lt; 0.01)</td>
</tr>
<tr>
<td>Pos3</td>
<td>−75.12 to −75.54</td>
<td>−22.12</td>
<td>+1.91 (+1.65)</td>
<td>0.26 (p &lt; 0.01)</td>
</tr>
<tr>
<td>Pos4</td>
<td>−77.84 to −78.04</td>
<td>−21.65</td>
<td>+2.16 (+2.46)</td>
<td>0.24 (p &lt; 0.01)</td>
</tr>
</tbody>
</table>

Note: Stratigraphic position is measured in meters below the Cretaceous Hell Creek–Paleogene Fort Union (Khc-PgFtu) formational contact. The magnitude of the carbon isotope excursion is the difference between the absolute value of the excursion and the five-point running average value at that stratigraphic horizon; parenthetical values are the difference between the absolute value of the excursion and the absolute value of the sample immediately below the excursion. Standard error is the error of the five-point running average at that stratigraphic horizon; parenthetical value is the p-value at which we reject the null hypothesis that the excursion value is within the range of variation expressed by the five samples stratigraphically surrounding the excursion.
Carbon isotope stratigraphy and correlation of megafossil localities in the Hell Creek Formation, Montana, USA

Figure 4. Carbon isotope correlation of upper Hell Creek Formation paleontological localities from the central portion of the Hell Creek type area—Mushroom Butte, Bone Hollow, Helen’s Leaves, Rick’s Place, and Smurphy’s Guess—to the upper portion of the Herman Ridge section. Carbon isotope values from samples with ≤0.1% organic carbon are marked with filled polygons. The −2‰ to −3‰ carbon isotope excursion marks the Cretaceous-Paleogene boundary in all localities. This interpretation of the Cretaceous-Paleogene boundary is used as a tie point across all sections. At Rick’s Place, the carbon isotope excursion interpreted to represent the Cretaceous-Paleogene boundary occurred immediately above a clay layer containing an iridium (Ir) and shocked mineral anomaly (Bohor et al., 1984). A second negative excursion (Neg1) ~3–4 m below the Cretaceous-Paleogene excursion was also identified in these sections. Khc—Cretaceous Hell Creek Formation, PgFtu—Paleogene Tullock Member of the Fort Union Formation.
Bone Hollow

The Bone Hollow locality (Fig. 1; Appendix 1) is not associated with a plant megafossil locality, but it does include several productive Lancian vertebrate sites (e.g., UCMP V72199, V72200, V84047). Bone Hollow was sampled in 1997 and was among the first localities in the Hell Creek Formation type area that we studied with carbon isotopes. At that time, we were still experimenting with stratigraphic sampling distance and field protocols. Although the section captures the top of the Hell Creek Formation with the initiation of lignite and variegated pond deposition (Archibald, 1982; Fastovsky, 1987) characteristic of the Hell Creek–Fort Union formational contact, the Cretaceous–Paleogene boundary negative carbon isotope excursion is not fully sampled. We provisionally locate the negative portion of the excursion in the topmost sample of the Hell Creek–Fort Union contact lignite (Fig. 4), but because we have no samples above it, we cannot be confident that we captured its minimum value, and we did not capture the positive recovery characteristic of all excursions. The magnitude of the uppermost sample (−25.33‰) is higher than typical of the Cretaceous–Paleogene boundary excursion, which supports the possibility that we did not sample the excursion fully. Therefore, this correlation is provisional. Alternatively, the excursion at −2.80 m (interpreted as Neg1 in Fig. 4) might be the Cretaceous–Paleogene boundary excursion. We do not favor this interpretation because the absolute value of this excursion (−25.67‰) is also higher than typical of the Cretaceous–Paleogene boundary excursion, and this excursion is fully sampled. Moreover, the absolute value of this excursion is similar to that of Neg1 in the Herman Ridge section (Table 2), and it occurs several meters below the Hell Creek–Fort Union formational contact, as is typical of Neg1 in both the Herman Ridge section and the marine sections in which it appears (e.g., the Kjølby Gaard section in Denmark; Kaminski and Malmgren, 1989).

Helen’s Leaves

At the Helen’s Leaves locality (Fig. 1; Appendix 1), a −2.2‰ carbon isotope excursion at the top of the upper lignite split was interpreted as the Cretaceous–Paleogene boundary (Fig. 4). We also observed the Neg1 excursion −2.5 m below the Cretaceous–Paleogene boundary (Fig. 4). Both of these excursions matched those reported in the Herman Ridge section (Table 2) and at other Cretaceous–Paleogene boundary sites in the area; Arens and Jahren, 2000) in both absolute value and magnitude. However, in the Hell Creek reference section, the Cretaceous–Paleogene boundary carbon isotopic excursion occurs below the Hell Creek–Fort Union formational contact, while the excursion appears above the contact at the Helen’s Leaves locality. Helen’s Leaves yields four plant megafossil horizons. The lower pair (Fig. 4; two closely associated plant-bearing horizons indicated by a single symbol) included horizons collected at the bottom and top of a 1.60-m-thick gray mudstone sandwiched between lignite splits. Since the lower of these lignites is the lowest traceable lignite below the onset of variegated deposits and above swelling clay beds, we place the Hell Creek–Fort Union formation contact at its base. Thus, these collections represent floras of latest Cretaceous age preserved in Fort Union rocks, after the local change in substrate (from well-drained Hell Creek Formation sediments to Fort Union wetlands) but before the terminal Cretaceous ecological catastrophe. As such, they may be analogous in time and environment to the FOU floras of North Dakota (Johnson, 2002; Nichols and Johnson, 2008). The upper pair of plant localities (Fig. 4; two closely associated plant-bearing horizons indicated by a single symbol) occurred at the top and bottom of a 1.90-m-thick unit of interbedded silty mudstone and siltstone with plane-parallel lamination and horizons of ironstone concretions. These represented deposition in the Fort Union Formation and were inferred to be of Paleogene age. Thus, this locality provides a potentially useful comparison of floras from similar depositional environments before and after the Cretaceous–Paleogene extinction. This site also provides another example illustrating the initiation of lignite deposition prior to the Cretaceous–Paleogene boundary in eastern Montana.

Rick’s Place

An iridium- and shocked mineral–bearing impact horizon is present at this locality (Bohor et al., 1984; Fastovsky, 1987), and it can be used to corroborate the carbon isotope curve. We interpreted a −2.5‰ carbon isotope excursion immediately above the impact layer as the Cretaceous–Paleogene boundary carbon isotope excursion (Fig. 4). The plant megafossils here occurred ~10 cm above the impact horizon and immediately above the Hell Creek–Fort Union formational contact. Thus, this collection represents plants from Fort Union facies deposited in Paleogene time.

Smurphy’s Guess

At the Smurphy’s Guess locality (Fig. 1; Appendix 1), we interpreted a −2‰ carbon isotope excursion that peaks in the first centimeters of the basal Fort Union lignite as the Cretaceous–Paleogene boundary excursion (Fig. 4). The Neg1 excursion also appeared ~4 m below the Cretaceous–Paleogene boundary and Hell Creek–Fort Union formational contact, a greater distance than observed in the Herman Ridge section. This is a significantly greater stratigraphic distance than observed at Herman Ridge, Bone Hollow, or Helen’s Leaves. At Rick’s Place, the Neg1 excursion (Fig. 4) occurred in a thick unit of blocky gray mudstone that displayed little paleosol development. This mudstone may represent a locally high rate of deposition that produced an expanded section. Leaves were preserved in an 80-cm-thick black mudstone that was laminated at the top. Therefore, this locality represents vegetation from Hell Creek Formation–style deposition and latest Cretaceous time, but it is older than floras from the Cretaceous localities discussed previously.
Next, we correlate localities in lower Hell Creek Formation deposits from the central portion of the type area. The apparently cyclic trend toward lower and then higher δ13C values between the base of the Hell Creek Formation in the reference section and approximately +15 m, and the Neg6 excursion were particularly useful for correlating in this part of the section. Figure 5 presents hypothesized correlations for four fossil-bearing localities in the lower portion of the Hell Creek Formation.

PDM

The PDM locality (Fig. 1; Appendix 1) yielded several horizons of well-preserved leaf and cone material (discussed in detail in Arens and Allen, this volume) and a partial hadrosaur skeleton (MOR HC-278). At this locality, the contact of the Hell Creek Formation with the underlying Fox Hills Formation (the Colgate Member was not present at the PDM locality) occurred ~10 m below the plant megafossil horizons and ~8 m below the dinosaur quarry, although terrain thwarted precise measurement. The Neg6 excursion, which was characterized by two low values separated by a higher value (lower dashed line in Fig. 5), was preserved in the PDM section. In the Herman Ridge section, the minimum value of the Neg6 excursion was −27.5‰. At the PDM locality, the δ13C value of the proposed correlation point was −27.9‰; the similarity in these absolute values supports the correlation. The Neg5 excursion (upper dashed line in Fig. 5) had an absolute value of −25.6‰ in the reference section and an absolute value of −26.0‰ in the PDM section. We also made a tentative correlation with the Pos4 excursion at the highest values of the positive trend noted between Neg6 and Neg5. If the correlation to Pos4 is correct, there was significant missing time between the Pos4 event and the Neg5 excursion at PDM, relative to the Herman Ridge section. This interpretation is supported by the moderately well-developed paleosols in the topmost 2.5 m of the PDM section. If this correlation is correct, the plant megafossil-bearing horizons (Arens and Allen, this volume) are 2–3 m below the Neg6 excursion (lower dashed line in Fig. 5). Furthermore, the Hell Creek–Fox Hills formational contact lies ~10–11 m below the Neg6 excursion (lower dashed line in Fig. 5). This suggests similar rates of deposition between the Herman Ridge section and PDM.

Fisk II

The Fisk II locality (Fig. 1; Appendix 1) also included the Neg6 carbon isotope excursion, with which it can be correlated to nearby sections and to the Herman Ridge reference section (Fig. 5). In the Fisk II section, the maximum δ13C value of the Neg6 excursion was −26.9‰, compared to −26.7‰ at Fisk III and −27.5‰ in the Herman Ridge section. The similarity in absolute value of this excursion between Fisk III and Fisk II suggested a sound correlation. Furthermore, a similar positive excursion (Pos4 in Fig. 5) of −22.8‰ and −21.9‰ in Fisk III and Fisk II, respectively, that occurred 4 m and 6 m above the Neg6 excursion, respectively, supported the correlation. The absolute value of the Pos4 excursion in the Herman Ridge section was −21.7‰, which matches that of Fisk II, further validating this correlation. If this correlation is correct, the plant megafossil locality at Fisk II occurs ~1 m above the Pos4 excursion and thus significantly above the floras of Fisk III and PDM. Furthermore, the absence of the Neg5 excursion (upper dashed line in Fig. 5) in the Fisk II section suggests depositional rates higher than those at Fisk III or an interval of missing time.

Celeste’s Metasequoia

The short section at the Celeste’s Metasequoia locality (Fig. 1; Appendix 1) preserved only the Neg6 excursion (lower dashed line in Fig. 5) with an absolute δ13C value of −27.8‰, which compared favorably with the correlative excursion in the Herman Ridge section (δ13C value = −27.5‰). This negative excursion was followed by a generally positive trend, but however, the Neg6 excursion at Fisk III registers the lowest values in this portion of the section, which corresponds with the pattern observed in the Herman Ridge section. The Neg6 excursion at Fisk III also began the positive portion of the cyclic variation in δ13C values up section, which also corresponds to the pattern at Herman Ridge. These observations corroborate our proposed correlation. We also note the Pos3 excursion at the low point in the cyclic variation and the Pos4 excursion at the high point of the cyclic variation (Fig. 5). The Pos3 excursion had an absolute value of −23.31‰ in the Fisk III section compared to −22.12‰ in the Herman Ridge section; the Pos4 excursion had an absolute value of −22.8‰ in the Fisk III section compared to −21.7‰ in the Herman Ridge section. The magnitude of these features also supports provisional correlation. Finally, a negative δ13C value of −26.6‰ was provisionally correlated to the Neg5 excursion (δ13C = −25.6‰ in the Herman Ridge section; upper dashed line in Fig. 5). If this correlation is correct, the Fisk III plant megafossil locality is ~10.5 m below the Neg6 excursion. In the Herman Ridge section, this stratigraphic position would coincide with the Hell Creek–Fox Hills formational contact. Since the measured stratigraphic section at Fisk III includes 7 m of strata below the excursion, and the lower contact is not exposed, we infer that the basal Hell Creek Formation sediments are thicker at the Fisk III locality compared to the Herman Ridge locality and PDM.
Figure 5. Carbon isotope correlation of lower Hell Creek Formation paleontological localities—PDM, Fisk III, Fisk II, and Celeste’s *Metasequoia*—to the lower portion of the Herman Ridge section. Carbon isotope values from samples with ≤0.1% organic carbon are marked with filled polygons. A negative excursion (Neg6, δ¹³C = −27.5‰) at the apex of positive to negative trend between 0 m and 18 m in the reference section (lower dashed line) was a primary tie point. A second negative excursion (Neg5, δ¹³C = −26‰, upper dashed line) served as a second point of correlation. This upper excursion was not sampled in Fisk II or Celeste’s *Metasequoia* localities. We hypothesized that it occurred stratigraphically above the section sampled. Alternatively, it may indicate missing time in these sections.
no δ13C values reached the −21‰ to −22‰ levels suggestive of the Pos4 excursion. If this interpretation is correct, plant megafossils at Celeste’s *Metasequoia* were deposited after the Neg6 excursion and before the Pos4 excursion. At Fisk III, 4 m of sediment separate these chemostratigraphic markers. At Fisk II, the stratigraphic distance is 6 m. Here, more than 12 m of sediment separate the Neg6 excursion from the top of the section, at which point the highest values of the Pos4 excursion have not been reached. This suggests high sedimentation rates characterized this locality.

The final group of localities included two in easternmost Garfield County and the Z-Line Quarry in western McCone County. These localities represent upper Hell Creek Formation and Fort Union Formation sites. Proposed correlations are presented in Figure 6.

**Constenius**

The Constenius locality (Fig. 1; Appendix 1) included a Puercan-age vertebrate microfossil site (UCMP V 96268 ~3 m...
below the Hell Creek–Fort Union formational contact, and a plant megafossil horizon was noted ~6 m above the formational contact. A sample ~5.5 m from the base of the lowermost lignite below variegated Fort Union deposits at this locality showed a modest (~1.3‰) negative carbon isotope excursion that we have provisionally interpreted as the Cretaceous-Paleogene boundary excursion. This feature is bracketed by dinosaur remains below and a Pu1 fauna above. This excursion is of lower magnitude than is typical for the Cretaceous-Paleogene boundary excursion in this region, but it is within the range of values reported for other sections where the stratigraphic placement of the Cretaceous-Paleogene boundary is diagnosed by iridium, shocked minerals, and palynostratigraphy (Arens and Jahren, 2000). The absolute value of the excursion ($\delta^{13}C = -26.1\%$) is also within the range of values reported for the Cretaceous-Paleogene boundary excursion. If this correlation is correct, the lignite marking the Hell Creek–Fort Union formational contact is more than 5 m above the Cretaceous-Paleogene boundary, marking relatively late onset of lignite formation in this area. Plant megafossil localities are of Paleocene age. The carbon isotope curve below the Cretaceous-Paleogene boundary is noisy and defies interpretation.

**Wild Horse Basin**

The Wild Horse Basin section (Fig. 1; Appendix 1) preserved four horizons yielding plant megafossils (Fig. 6). The sandstone at the base of the section measured for this study (Fig. 6) also yielded Lancian vertebrates (UCMP V75178). At Wild Horse Basin, the Neg1 ($\delta^{13}C = -25.41\%$) excursion was ~15 m below the Hell Creek–Fort Union formational contact, in contrast to ~3 m below the contact in the Herman Ridge section. This suggests a high sedimentation rate in this region compared to the Herman Ridge section. Thick horizons (1–4 m) of laminated and structureless mudstone in the upper meters of the Hell Creek Formation at Wild Horse Basin support this conclusion. These mudstones did not preserve rooting structures and may represent a single major flood event, or multiple smaller flood events separated by little time. This contrasts with the temporally correlative portion of the Herman Ridge section where paleosols had developed. The plant megafossil localities straddle the Neg1 excursion.

**Z-Line Quarry**

The Z-Line Quarry locality (Fig. 1; Appendix 1) preserved one horizon of plant megafossils and three nearby vertebrate microfossil localities, one representing a typically Lancian fauna (UCMP V84186) and two others including forms characteristic of early Puercan time (Pu1, UCMP V84193 and V84194; Fig. 6). These faunas bracketed the negative carbon isotope excursion interpreted as the Cretaceous-Paleogene boundary (~24.66‰) and corroborated the interpretation of this excursion as representative of the Cretaceous-Paleogene boundary, even in the absence of an iridium- and shocked mineral–bearing boundary clay. However, the absolute value of this excursion is much higher than that observed at the Herman Ridge section (~26.47‰; Table 2) and at other confirmed Cretaceous-Paleogene boundary localities in the region (Arens and Jahren, 2000), where minimum absolute values for the negative excursion are generally less than ~26‰. This calls the utility of these features into question. An excursion we tentatively interpreted as Neg1 was preserved (Fig. 6) 2 m below the Cretaceous-Paleogene boundary excursion. It too had a much higher absolute value (~24.29‰) than that observed in the Herman Ridge section (~25.64‰; Table 2). However, the stratigraphic thickness separating the proposed Cretaceous-Paleogene and Neg1 excursions was similar to that observed in the Herman Ridge section and thus indicated a similar rate of sedimentation. If this correlation, which is supported by vertebrate microfossil data, is correct, the Z-Line flora represents a post-Cretaceous flora in Hell Creek facies, thus offering an opportunity for comparison with other localities in which Paleocene-age floras are more typically preserved in Fort Union variegated facies.

The Z-Line Quarry locality highlights two important points about the interpretation of carbon isotope data for the correlation of stratigraphic sections. First, matching only the pattern of secular variation (disparingly called “squiggle matching” by some) provides incomplete support for an interpretation. Absolute values and the magnitude of change associated with features such as excursions and shifts are important corroborating evidence. Second, interpretations are strongest when made in coordination with other lines of evidence, such as paleontology (in the case of the Z-Line Quarry) or rare earth geochemistry (in the case of Rick’s Place, where the Ir and shocked mineral anomaly associated with the Cretaceous-Paleogene boundary is preserved).

**DISCUSSION**

The focus of this research has been to create a chronostratigraphic context in which to seriate fossil localities in time. Such a framework is essential for questions of floral, faunal, and environmental change through Hell Creek time and across the Cretaceous-Paleogene boundary. Precision and accuracy in the correlation of fossil localities around the Cretaceous-Paleogene boundary are essential if we wish to consider the relative roles of environmental change (well-drained Hell Creek floodplains vs. Fort Union wetlands), climate change (e.g., Wilf et al., 2003), and the terminal-Cretaceous bolide impact in producing biotic change.

Most previous workers in the Hell Creek have documented the stratigraphic position of fossil localities relative to the base or top of the formation. While this approach is a useful first approximation, both the base and the top of the Hell Creek Formation are known to be diachronous across the basin (Archibald et al., 1982; Fastovsky and Dott, 1986; Fastovsky, 1987; Swisher et al., 1993; Pearson et al., 2001), and sedimentation rates are expected to vary regionally. Considering only the localities studied here, we noted significant variation in the placement of the Hell
Carbon isotope stratigraphy and correlation of megafossil localities in the Hell Creek Formation, Montana, USA

Origin of Carbon Isotope Features in the Hell Creek Formation

Identifying the sources of the carbon isotope variation observed within the Hell Creek Formation is beyond the scope of this study. However, some general comments can be made. The −1.5‰ to −2‰ Cretaceous-Paleogene boundary negative excursion has been well documented in marine (e.g., Hsu et al., 1982; Perch-Nielsen et al., 1982; Zachos and Arthur, 1986; Keller and Lindinger, 1989; Stott and Kennett, 1989, 1990; Zachos et al., 1992; Keller et al., 1996; D’Hondt, 1998) and terrestrial sections (e.g., Schimmelmann and DeNiro, 1984; Arens and Jahren, 2000, 2002; Beerling et al., 2001; Gardner and Golmour, 2002; Hasegawa et al., 2003). The excursion has been attributed to cessation of primary productivity in the surface ocean following the Cretaceous-Paleogene bolide impact (Hsu et al., 1982; Zachos and Arthur, 1986; D’Hondt, 1998), to the addition of isotopically depleted carbon from the burning of terrestrial biomass (Kump, 1991; Ivany and Salawitch, 1993), and to the introduction of carbon from gas hydrates disturbed by the bolide impact (Day and Maslin, 2001).

Beyond the well-studied Cretaceous-Paleogene boundary negative excursion, it was impossible, with the available data, to attribute any of the Hell Creek Formation carbon isotope excursions to described events. However, general statements can be made with respect to carbon sources and sinks that might drive the isotopic composition of atmospheric carbon dioxide. Several carbon reservoirs have the potential to move significant amounts of carbon into or out of the atmospheric reservoir. These include volcanogenic CO\textsubscript{2}, continental shelf gas hydrates, organic matter, and weathering.

Volcanogenic CO\textsubscript{2} varies in isotopic composition between −2‰ and −8‰ (Allard, 1982; Taylor, 1986). Carbon dioxide injected into the atmosphere as part of latest Maastrichtian and Danian Deccan Trap volcanism could have accounted for negative carbon isotope excursions and triggered the climatic warming observed to begin ∼500 k.y. before the end of the Cretaceous Period (Wilf et al., 2003; Thibault and Gardin, 2007). Recent work showed that the Deccan volcanics were emplaced during three eruptive episodes: (1) ca. 67.5 ± 1 Ma near the C30r/C30n transition, (2) a larger phase in which 80% of the magma associated with Deccan Traps was erupted during a period that began during C29r and ended at the Cretaceous-Paleogene boundary, and (3) spanning the C29r/C29n transition in the Paleocene (Chenet et al., 2007, 2008, 2009; Keller et al., 2008, 2009, 2011). The beginning of the second eruptive episode might account for the Neg1 excursion observed in our data and in other marine sections (e.g., Kaminski and Malmgren, 1989). However, this hypothesis would require an independent line of evidence capable of correlating between the volcanic events and the carbon isotope anomalies identified in marine and terrestrial sediments.

Gas hydrates have been implicated in a variety of negative carbon isotope excursions (e.g., Dickens et al., 1995, 1997; Jahren et al., 2001; Beerling et al., 2002). Carbon in gas hydrates...
is extremely depleted in $^{13}$C ($\delta^{13}$C = −60‰; Kvenvolden, 1993), so a small-volume release could generate a significant negative excursion (Jahren et al., 2001). Methane hydrate reservoirs on the continental shelf and slope are vulnerable during sea-level lowstand. We hypothesize that the large-magnitude negative carbon isotope excursions Neg6 and Neg3 (Table 2) may be associated with the regressive trend inferred in the lower half of the Hell Creek Formation (Murphy et al., 2002). This hypothesis could be tested by looking for an association between these carbon isotopic events and maximum regressive surfaces identified within the Hell Creek Formation by sequence stratigraphic analysis.

Over short geological time scales, climate exerts significant control on the size of the terrestrial organic matter (TOM) carbon reservoir and the amount of atmospheric carbon dioxide removed by weathering. Growth of the terrestrial biosphere and associated additions to the TOM reservoir might result in a short-term increase in the $\delta^{13}$C value of atmospheric carbon dioxide (average standing biomass $\delta^{13}$C = −25‰; average soil organic carbon $\delta^{13}$C = −27‰; Peng et al., 1983; Cerling et al., 1991). In addition, if this photosynthetically fixed carbon was removed from the active carbon cycle through root respiration, equilibration with soil water, weathering, and transport, $^{12}$C may be removed from the atmosphere over the longer term. We note that wet climates and rising water tables generally promote the accumulation of organic matter in the TOM reservoir, as well as speed weathering reactions. In contrast, the $\delta^{13}$C value of atmospheric carbon dioxide could decrease in the short term if terrestrial carbon were returned to the atmosphere by biomass burning (suggested for the Cretaceous-Paleogene boundary; Ivany and Salawitch, 1993), by deforestation, or by enhanced oxidation of soil organic matter. All of these phenomena are strongly associated with climatic drying. Despite these generalizations, we currently have no independent lines of evidence linking specific patterns within the Hell Creek Formation carbon isotope reference curve with paleoprecipitation patterns.

**CONCLUSIONS AND FUTURE RESEARCH**

In this paper, we constructed a high-resolution carbon isotope reference curve for the entire Hell Creek Formation and used this reference to correlate widely separated fossil-bearing sections (Fig. 7). We recognized six negative carbon isotope excursions in addition to the Cretaceous–Paleogene excursion that proved useful for correlating among sections. We also recognized four positive carbon isotope excursions that may provide supporting evidence for correlation, but which may be influenced by residual inorganic carbon. Some of these features (e.g., the Cretaceous–Paleogene carbon isotope anomaly and Neg1) have parallels in the marine record, indicating that they represented...
global variations in carbon cycling. However, most marine sections lack the temporal and sampling resolution of the Hell Creek Formation terrestrial section. Therefore, a detailed comparison of the marine and terrestrial record awaits additional data.

The work described herein suggests several future directions. First, additional complete sections through the Hell Creek Formation will be needed to corroborate the chemostratigraphic markers described here. A high-resolution chemostratigraphic analysis should be part of the documentation of the newly proposed stratotype section (Hartman et al., this volume). Such an analysis would substantiate the Hell Creek Formation carbon isotope reference curve and further test its utility in regional correlation. Analysis of the stratotype would also allow the chemostratigraphic framework to be placed in a magnetostratigraphic and sequence stratigraphic context, which would allow testing of some of the mechanistic hypotheses described here. Second, additional fossil-bearing localities can be added to the chemostratigraphic framework to better integrate the plant and animal records for the Hell Creek type area. Such sections should be sampled at high stratigraphic resolution—a minimum of 10 cm intervals—to capture details of secular variation. Such additional analyses would also allow documentation of spatial variation in sedimentation rate suggested by our preliminary analyses. This may elucidate spatial and temporal variation in accommodation and/or paleotopography.

ACKNOWLEDGMENTS

Fieldwork and analyses for some of the localities described herein were supported by National Science Foundation grant EAR-0241190 to Arens. Additional support for fieldwork was provided by the University of California Museum of Paleontology. W.M. Hagopian and B. Halfman provided invaluable service in the laboratory. This manuscript was significantly improved through conversations with, comments from, and/or formal reviews by W.A. Clemens, M. Clementz, D. Fastovsky, J. Schmitt, and G.P. Wilson.

APPENDIX 1. LOCALITY INFORMATION

Herman Ridge Section (Arens’s field notes also refer to this section as Loomis Overlook because access traverses the Loomis ranch). Garfield County, Montana, Pine Grove School quadrangle, SW ¼ NE ¼ SE sec. 5, T. 21 N., R. 33 E.; UTM 13T 0310914E, 5276282N; 47°36′44.3″N, 107°30′58.0″W (top of section); NAD83CONUS. Hell Creek Formation, top of the section begins at the Cretaceous Hell Creek–Paleogene Fort Union (Khc-PgFu) formational contact, 92 m above base of Khc, elevation ~940 m (3085 ft).

Bone Hollow (associated with UCMF V 72199). Garfield County, Montana, Trumbo Ranch quadrangle, sec. 34, T. 21 N., R. 36 E.; UTM 13T 0343247E, 5266783N; 47°32′8.0″N, 107°45′58.0″W; NAD83CONUS. Hell Creek Formation, stratigraphic section includes Khc-PgFu contact, elevation ~835 m (2738 ft).

UCMP PB 99056 Celeste’s Metasequoia. Garfield County, Montana, Peterson Point quadrangle, NW ¼ SW ¼ sec. 36, T. 22 N., R. 37 E.; UTM 13T 0356602E, 5276476N; 47°37′32.4″N, 106°54′59.7″W; NAD83CONUS. Hell Creek Formation, neither top nor bottom of the formation are visible from this locality, elevation ~762 m (2500 ft).

Constenius (associated with UCMP V 96268). Garfield County, Montana, Flat Creek School quadrangle, SW ¼ NE ¼ SE ¼ NE sec. 10, T. 21 N., R. 41 E.; UTM 13T 0392127E, 5272594N; 47°35′52.0″W, 106°26′9.0″N; NAD83CONUS. The Lancian-age fauna noted in Figure 6 consists primarily of dinosaur remains that were not collected. Plant megafossils are located in Fort Union Formation ~6.7 m above the Khc-PgFu contact, elevation ~771 m (2530 ft). This flora has not yet been collected.

UCMP PB 99017 Fisk II. Garfield County, Montana, Meloney Hill quadrangle, NW ¼, SE ¼, NW ¼ sec. 14, T. 21 N., R. 37 E.; UTM 13T 0354109E, 5271722N; 47°34′57.0″N, 106°56′24.7″W; NAD83CONUS. Hell Creek Formation, neither the top nor the bottom of the formation are visible from this locality, elevation ~788 m (2585 ft).

UCMP PB 99020 Fisk III. Garfield County, Montana, Meloney Hill quadrangle, SE ¼ NW ¼ SE NW ¼ sec. 14, T. 21 N., R. 37 E.; UTM 13T 0354279E, 5271577N; 47°34′52.4″N, 106°56′16.4″W; NAD83CONUS. Hell Creek Formation, neither the top nor the bottom of the formation are visible from this locality, elevation ~760 m (2492 ft).

UCMP PB 99023 Helen’s Leaves. Garfield County, Montana, Trumbo Ranch quadrangle, NW ¼ NE ¼ sec. 4, T. 20 N., R. 35 E.; UTM 13T 0306413E, 5265925N; 47°31′44.6″N, 107°00′50.0″W; NAD83CONUS. Fort Union Formation, Tullock Member. Fort Union–Paleogene Fort Union (Khc-PgFtu) formational contact, ~92 m above the Khc-PgFu contact; upper 8 m above Khc-PgFu contact, elevation ~850 m (2790 ft). This locality was originally named the Brownie Butte Flora Localite because of its proximity to a named butte across the road and to the northwest of the locality. However, because this name has been used for other informal field sites, it was renamed to avoid confusion.

UCMP PB 99059 Mushroom Butte. Garfield County, Montana, Hells Hollow quadrangle, SW ¼ NE ¼ sec. 36, T. 21 N., R. 35 E.; UTM 13T 0336221E, 5265712N; 47°31′26.9″N, 107°10′32.5″W; NAD83CONUS. Hell Creek Formation, megaflora localities ~2 m below the Khc-PgFu formational contact, elevation ~881 m (2891 ft).

UCMP PB 99057 PDM (associated with MOR HC-278). Garfield County, Montana, Meloney Hill quadrangle, NE ¼ NW ¼ sec. 4, T. 21 N., R. 37 E.; UTM 13T 0351470E, 5275273N; 47°36′50.0″N, 106°58′35.4″W; NAD83CONUS. Hell Creek Formation, series of megafossil-bearing horizons between 8 and 9 m above base of Khc, elevation ~785 m (2575 ft).

Rick’s Place Iridium Quarry (UCMF V 73098). Garfield County, Montana, Trumbo Ranch quadrangle, SW ¼ SW ¼ SW ¼ SW ¼ sec. 32, T. 21 N., R. 37 E.; UTM 13T 0348880E, 5265889N; 47°33′0.9″N, 107°02′28.7″W; NAD83CONUS. Fort Union Formation, Tullock Member, megaflora locality ~1 m above Khc-PgFu contact, elevation ~851 m (2790 ft). The Cretaceous–Paleogene boundary clay bearing an Ir and shocked mineral signature was identified at this locality (Bohor et al., 1984). The pinkish boundary clay was observed during the sampling for this paper.

UCMP PB 99010 Smurphy’s Guess (associated with PB 99011). Garfield County, Montana, Meloney Hill quadrangle, NW ¼ NW ¼ SE ¼ sec. 25, T. 21 N., R. 37 E.; UTM 13T 0356097E, 5268088N; 47°33′0.9″N, 106°54′45.3″W; NAD83CONUS. Hell Creek Formation, ~13.5 m below Khc-PgFu contact, elevation ~835 m (2738 ft).

UCMP PB 97018 Wild Horse Basin (associated with PB 97019 and V75178). Garfield County, Montana, Short Creek quadrangle, NE ¼ SE ¼ SW ¼ sec. 2, T. 21 N., R. 42 E.; UTM 13T 0402665E, 5272901N; 47°36′7.9″N, 106°17′14.7″W; NAD83CONUS. Hell Creek Formation, series of fossil-bearing localities 12–16 m below the Khc-PgFu contact, elevation ~725 m (2380 ft).

Z-Line Quarry (associated with UCMF V 84193). McCoine County, Montana, Nelson Creek Bay quadrangle, sec. 4, T. 21 N., R. 43 E.; UTM 13T 0400578E, 5265289N; 47°36′31.8″N, 106°12′23.3″W; NAD83CONUS. Hell Creek Formation, ~2 m below Khc-PgFu contact, elevation ~698 m (2290 ft).
APPENDIX 2. SIDERITE SOLUBILITY IN 1 M HCL

Introduction

Removing inorganic carbon from geologic samples before carbon isotopic analysis is essential to accurate measurements of the carbon isotopic composition of plant-derived carbon used in chemostatigraphic correlation (Arens and Jahren, 2000, 2002; Arens et al., 2000). Even a small amount of inorganic carbon left behind in the sample could alter the $^{13}$C/$^{12}$C ratio toward greater values. As little as 0.5% residual inorganic carbon ($\delta^{13}$C = $-2\%$o) by weight could render the resulting carbon isotopic values up to 1% more positive than they would be if all inorganic carbon had been removed (Larson et al., 2008). Our standard preparation protocol removes inorganic carbon by acidification in a large volume of 1 M HCl relative to the sample volume, collected by decanting of the acid. Larson et al. (2008) speculated that siderite may be left behind by some acidification methods, thus introducing inaccuracy in the resulting organic carbon isotopic measurements.

The diagenetic carbonate mineral siderite (FeCO$_3$) is a ubiquitous component of Hell Creek Formation sediments. Siderite is significantly less soluble (log K = $-10.45$) than calcite (log K = $-8.48$), the other common source of sedimentary inorganic carbon in Hell Creek Formation samples. Consequently, residual siderite could, at best, introduce random error in our results or, at worst, produce false positive isotopic excursions. We therefore experimentally tested our preparation protocol to determine the extent to which siderite might be left behind in samples.

Material and Methods

Siderite mineral (Ward’s Scientific, Rochester, New York) was washed, dried, crushed, weighed (balance precision ±0.01 g), and acidified in 1 M HCl overnight (12 h), following the protocol used to prepare geologic samples for carbon isotopic analysis described in this paper. The resulting preparation was centrifuged, residual acid was decanted, and the sample rinsed in deionized water. The pellet was washed, dried, crushed, weighed (balance precision ±0.01 g), and acidified in 1 M HCl overnight (12 h), following the protocol used to prepare geologic samples for carbon isotopic analysis described in this paper. The resulting preparation was centrifuged, residual acid was decanted, and the sample rinsed in deionized water. The pellet was dried and weighed. Mass change was calculated as a percent of dry weight.

Results

The following table presents data on weight percent loss by dissolution in 1 M HCl.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dry weight before acidification (g)</th>
<th>Dry weight after acidification (g)</th>
<th>Weight percent loss on acidification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.79 ± 0.01</td>
<td>0.29 ± 0.01</td>
<td>91.6</td>
</tr>
<tr>
<td>2</td>
<td>2.67 ± 0.01</td>
<td>0.14 ± 0.01</td>
<td>94.8</td>
</tr>
<tr>
<td>3</td>
<td>1.92 ± 0.01</td>
<td>0.07 ± 0.01</td>
<td>96.4</td>
</tr>
<tr>
<td>4</td>
<td>2.72 ± 0.01</td>
<td>0.24 ± 0.01</td>
<td>91.8</td>
</tr>
<tr>
<td>5</td>
<td>2.09 ± 0.01</td>
<td>0.21 ± 0.01</td>
<td>90.0</td>
</tr>
<tr>
<td>6</td>
<td>2.89 ± 0.01</td>
<td>0.29 ± 0.01</td>
<td>90.0</td>
</tr>
<tr>
<td>7</td>
<td>2.30 ± 0.01</td>
<td>0.19 ± 0.01</td>
<td>91.8</td>
</tr>
<tr>
<td>8</td>
<td>1.82 ± 0.01</td>
<td>0.12 ± 0.01</td>
<td>93.4</td>
</tr>
<tr>
<td>9</td>
<td>2.58 ± 0.01</td>
<td>0.15 ± 0.01</td>
<td>94.2</td>
</tr>
<tr>
<td>10</td>
<td>1.67 ± 0.01</td>
<td>0.07 ± 0.01</td>
<td>95.8</td>
</tr>
<tr>
<td>Average</td>
<td>2.35 ± 0.44</td>
<td>0.18 ± 0.08</td>
<td>92.7 ± 2.5</td>
</tr>
</tbody>
</table>

Conclusion

Approximately 93% of siderite was removed by dissolution in 1 M HCl using the decant method. Since a relatively small amount (12%) of this remaining mass is inorganic carbon, it seems unlikely that residual siderite would significantly alter carbon isotope measurements. However, this question bears more comprehensive investigation.

REFERENCES CITED


Carbon isotope stratigraphy and correlation of megafossil localities in the Hell Creek Formation, Montana, USA


