Stratigraphic evaluation of reservoir and seal in a natural CO_2 field: Lower Paleozoic, Moxa Arch, southwest Wyoming

Ranie Lynds[1*], Erin Campbell-Stone[1], Thomas P. Becker[2], and Carol D. Frost[1]

[1]*Department of Geology and Geophysics, University of Wyoming, 1000 E. University Ave., Laramie, Wyoming 82071, U.S.A.*

[2]*ExxonMobil Production Company, 396 West Greens Road, Houston, Texas 77067, U.S.A.*

* Correspondence should be addressed to: lynds@uwyo.edu

ABSTRACT

The Moxa Arch in the Greater Green River Basin, southwestern Wyoming, hosts two potential reservoirs for CO_2 sequestration. The Bighorn Dolomite and Madison Limestone are interpreted to be independent reservoirs based on differing CO_2 compositions and production histories; the two reservoirs are separated by Devonian carbonates, siliciclastic rocks, and evaporites.

On the Moxa Arch, the Bighorn ranges in thickness from 67 to 120 m with porosities from 3 to 15 percent. The massive buff-colored Steamboat Point Member comprises the bulk of the subsurface Bighorn in southwest Wyoming. Mottled dolostone (light-colored patches with higher porosity and dark-colored patches with lower porosity) is very common and is presumably the result of preferential early dolomitization of bioturbation. Core study suggests that this factor affects gas saturation and storage in this extensive reservoir.

The Lower Member of the Jefferson Formation is the most probable seal within the Devonian stratigraphy. Strata of this member are interpreted to have been deposited in a shallow basin semi-isolated from the deeper marine environment to the west. $^{87}Sr/^{86}Sr$ isotopic analyses of anhydrite sampled from Moxa Arch well cuttings support the interpretation of a depositional environment exposed to a mixture of seawater and freshwater. High-frequency relative sea level fluctuations superimposed on a gently sloping shelf produced alternating layers of marine carbonates, peritidal siliciclastic rocks, and evaporites. The evaporites are interpreted to seal CO_2 in the Bighorn Dolomite from the overlying Madison Limestone. The Lower Paleozoic strata on the Moxa Arch provide an effective trap-reservoir-seal combination for naturally occurring CO_2 with potential applications to future studies at analogous locations in the central Rocky Mountain Region.

KEYWORDS: anhydrite, Bighorn Dolomite, Darby Formation, Devonian, Greater Green River Basin, Jefferson Formation, Moxa Arch, Ordovician, reservoir, seal, sequestration, strontium, Wyoming.

INTRODUCTION

All proposed sites for geologic sequestration of anthropogenic CO_2 should share three basic characteristics: (1) a geometric subsurface trap that contains the gas within a manageable area, (2) a reservoir with sufficient porosity and permeability, and (3) an effective and robust overlying seal that can sustain a buoyant gas column for an appropriate time period (i.e., greater than 10,000 years; Lindeberg, 2002). These characteristics also typify conventional hydrocarbon accumulations, which have been long-studied in the petroleum industry. Such accumulations are commonly in traps that have held buoyant columns of gas, often for tens to hundreds of millions of years, demonstrating the feasibility of subsurface storage of carbon dioxide for geologically significant time periods.

Porosity and permeability are important factors for determining the storage capacity of the reservoir, its effectiveness as a reservoir, and the rate at which carbon dioxide can be put into the subsurface. Following Darcy's law, the permeability of the reservoir dictates the pressure required (and hence the energy required) to dispose of gas at a given rate. Capacity determination of a reservoir requires an understanding of variations in porosity and perme-

ability, which may compartmentalize a reservoir or create preferential pathways for flow. Depositional and post-depositional sedimentological features and structures need to be understood on a local and regional scale to properly determine the storage potential for CO_2.

The ability of the overlying, low-permeability sealing interval to hold a gas column is considered its sealing capacity (Downey, 1984). Assuming that the sealing interval is present over the entire extent of the trap, two independent factors determine capacity: mechanical strength and capillary entry pressure of the seal (e.g., Berg, 1975; Schowalter, 1979; Vavra et al., 1992; Gluyas and Swarbick, 2004). The mechanical capacity of a seal is compromised when the buoyant pressure on the unit exceeds its opening mode tensile strength (Secor, 1965; Lorenz et al., 1991). Capillary seal capacity is related to the pore throat size of the grains that comprise the seal and the capillary entry pressure required to displace water in the pore throats (e.g., Li and Wardlaw, 1986). The pressure required to overcome the interfacial surface tension rises exponentially as the pore throat diameter decreases (Vavra et al., 1992). Evaporite deposits make extraordinarily good seals (in the absence of fractures), in large part because they effectively do not have any pore space, meaning that failure requires a column to exceed the mechanical strength of the evaporite.

This paper focuses on the characteristics of an Ordovician reservoir and the overlying Devonian seal in a subsurface structure that has acted as a natural reservoir for carbon dioxide. The purposes of this study are to document what little information is known about the Bighorn Dolomite and the Devonian strata on the Moxa Arch in southwestern Wyoming, to provide the background information for a modeling framework, and to encourage future research into analogous viable reservoirs for CO_2 sequestration.

GEOLOGIC SETTING

The Greater Green River Basin in southwestern Wyoming and northern Utah possesses several natural gas fields with high concentrations of carbon dioxide. The crest of the Moxa Arch, culminating at the LaBarge Platform near LaBarge, Wyoming (Fig. 1), supports many producing fields. At the LaBarge

Field over 100 trillion cubic feet of natural gas are stored, much of it in the Mississippian Madison Limestone and the Ordovician Bighorn Dolomite (Stilwell, 1989). Between these two reservoirs are Devonian deposits that are commonly called the "Darby Formation" in the hydrocarbon industry. Gas produced from the Bighorn Dolomite is composed of 84.7 percent CO_2, whereas gas from the Madison Limestone contains 64.9 percent CO_2 (Stilwell, 1989). Production histories combined with CO_2 gas composition indicates the Bighorn and Madison are likely separate reservoirs.

The Mississippian Madison Limestone has been the subject of extensive investigation (see Thyne et al., 2010), yet relatively little is known about the subsurface Bighorn Dolomite and the overlying Devonian strata on the Moxa Arch. This can be attributed in part to economics: the Madison Limestone is the only Paleozoic unit on the Moxa Arch from which natural gas has been produced. As a result, numerous wells have penetrated the Madison interval, but few extend below it.

The Lower Paleozoic history of western Wyoming is closely tied to eustatic sea level changes. The paleogeography during this extended time was generally a north–south-oriented shoreline separating source terrains to the east and depositional basins to the west. During early Cambrian time, subaerial erosion of Precambrian igneous and metamorphic rocks provided siliciclastic sediment to nearshore areas while thick successions of deep-water strata accumulated in what is now Utah and Idaho (Boyd, 1993). Middle to Upper Cambrian (and possibly Lower Ordovician; Tice et al., 2002) deposits accumulated during an overall cratonward transgression of facies, resulting in a vertical succession consisting of the siliciclastic coarse-grained Flathead Sandstone, overlain by shale with interbedded limestone of the Gros Ventre Formation, and the capping mud-rich Gallatin Limestone. A major unconformity separates these Cambrian to Lower Ordovician strata from the Upper Ordovician Bighorn Dolomite. The latter formation is part of the record of perhaps the largest transgression in the history of North America (Boyd, 1993). Intervals of subaerial exposure following deposition of the Bighorn Dolomite resulted in thinning and/or removal of that formation in southern and eastern Wyoming, and removal of all evidence of the Silurian from western Wyoming (i.e., the interval
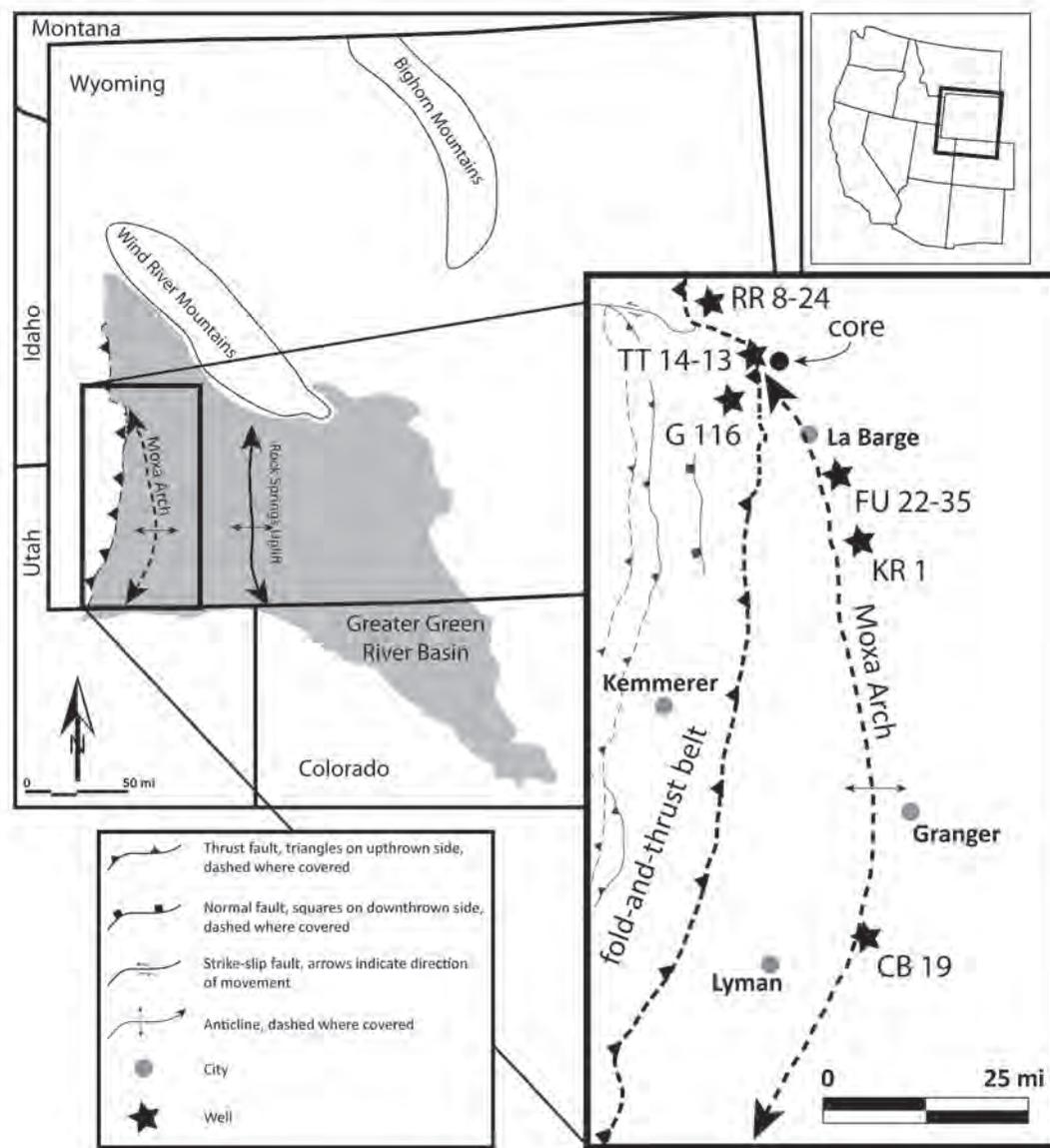
Figure 1. Location map of study area showing Wyoming and surrounding states, with the Greater Green River Basin highlighted in gray. Insert shows location of Moxa Arch, eastern front of Sevier fold-and-thrust belt, and key wells, core, and mountain ranges mentioned in text. Abbreviations are as follows: Riley Ridge 8-24 (RR 8-24), Tip Top F14-13 (TT 14-13), Graphite 116 (G 116), Fontanelle II Unit 22-35 (FU 22-35), Keller Rubow 1 (KR 1), and Church Buttes Unit 19 (CB 19).

between the second-order Tippecanoe and Kaskaskia transgressions; Sloss, 1963).

Laterally discontinuous lenses of Lower Devonian calcareous dolostone and conglomerate record terrestrial and shallow marine deposition (Sandberg and Mapel, 1967). Subsequent Middle Devonian regression and erosion produced a surface capped by an Upper Devonian transgressive sequence of limestones, dolostones, siliciclastics, and evaporites (Jefferson Formation and Three Forks Formation;

Benson, 1966). The Late Devonian was a time of numerous and cyclical sea level fluctuations possibly controlled by Gondwanan glaciation (Isaacson et al., 1999). The landscape was most likely a broad coastal area with a shallow sea, estuaries, lagoons, and a strong tidal influence. A major Mississippian transgression resulted in the greater than 300-m-thick Madison Limestone.

The Moxa Arch is a basement-involved anticline formed in the Late Cretaceous and Early Tertiary

during a two-phase growth process (Royse, 1993; Becker et al., 2010) that is generally associated with Sevier-Laramide orogenic deformation. This broad feature is 3.5 km high (Royse, 1993; Becker et al., 2010), with limbs dipping 0–5 degrees. It extends 200 km north-northwest from the Utah border to the eastern edge of the Wyoming fold-and-thrust belt (Fig. 1; Wach, 1977; Blackstone, 1990; Royse, 1993). Along much of its length, the Moxa Arch lacks emergent faults that displace any of the strata overlying the basement; the structure resembles a long, continuous, cylindrical, open fold (Wach, 1977; Royse, 1993). The LaBarge Platform represents the culmination of the Moxa Arch. The platform is located at its northern trace along its intersection with the thrust belt. The LaBarge Platform is characterized by a change in strike and the appearance of an emergent basement thrust fault along its southwestern edge (westward vergence) that displaces the overlying strata (Kraig et al., 1987; Royse, 1993).

BIGHORN DOLOMITE AS A CO$_2$ RESERVOIR

In subsurface reservoir characterization, an understanding of the degree of reservoir heterogeneity is directly proportional to the number of wells that penetrate the interval. Although there is a paucity of subsurface information about the Bighorn Dolomite on the Moxa Arch, the regional framework acquired from study of surrounding outcrops helps to constrain assumptions about the formation's age, extent, and stratal architecture.

Characteristics of the formation

The Bighorn Dolomite was deposited over a large portion of west-central North America as part of an extensive carbonate ramp (Wilson, 1975) that formed due to a major Late Ordovician (second-order Tippecanoe) transgression on the Laurentian cratonic shelf (Sloss, 1963; Boyd, 1993; Haq and Schutter, 2008). The Bighorn Dolomite crops out in southern Montana, far eastern Idaho, north-central Utah, and the northwestern half of Wyoming (Parker, 1950). The formation has a maximum thickness of 150 m (Teel, 1994) and is commonly divided into the basal Lander Sandstone Member, overlain by the Steamboat Point Member, the Leigh Member, and finally the Horseshoe Mountain Member, as defined by Goodwin (Fig. 2; 1964).

The Bighorn Dolomite is exposed throughout Wyoming as massive buff-colored cliffs. Although geologic study of this unit began as early as 1873, the first comprehensive investigation of the Bighorn Dolomite was by Darton (1906). Subsequent studies followed by Blackwelder (1913, 1918) and Tomlinson (1917). Many of these early papers, as well as several in the mid-1900s (e.g., Richards and Nieschmidt, 1957, 1961; Larimer, 1959), focused on the controversial age of the Bighorn Dolomite. Goodwin, in his 1964 summary of the literature, favored an age of Trenton-Maysville (late Middle Ordovician), but subsequent paleontological work (e.g., Sweet, 1979) has led to agreement on a Late Ordovician age for the formation. More recent work by

Zenger (1992) has concentrated on processes and controls on dolomitization of the formation.

According to Goodwin (1964), the basal Lander Sandstone Member ranges in thickness from 0 to 3 m, consists of medium- to coarse-grained sandstone with subrounded quartz grains, and can contain an abundance of shell fragments in isolated locations. This sandstone is primarily present in the Wind River Range near Lander, Wyoming, and grades into the overlying Steamboat Point Member. The Steamboat Point Member, 0 to 140 m thick, is a massive, mottled, buff-colored cliff-former (Fig. 3). It occurs from western to central Wyoming and
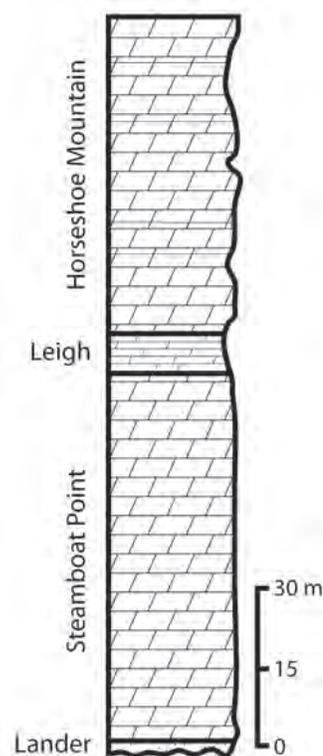
Figure 2. Generalized stratigraphic column showing members of the Ordovician Bighorn Dolomite in Wyoming, from Steamboat Point in the Bighorn Mountains. All lithologies are dolostone except for the Lander Sandstone. Modified from Zenger (1992).

throughout the eastern half of Montana and records a significant Late Ordovician transgression. The Leigh Member is 0 to 20 m thick, light to medium gray, very fine grained, "porcelaneous," and breaks with sub-conchoidal fractures. The Leigh Member can be found from northern Wyoming into southern Montana but was erosionally removed in the southern Wind River and Bighorn Mountains (Goodwin, 1964). The capping Horseshoe Mountain Member is primarily massive mottled dolostone, interrupted by layers of thin-bedded dolostone; it crops out in northern Wyoming and southeastern Montana where it is up to 64 m thick in the northern Bighorn Mountains. Goodwin (1964) attributed the variation in distribution and thickness of the Horseshoe Mountain Member to pre-Devonian erosion.

These previous studies were based on detailed examination of outcrops primarily located in the Bighorn Mountains and the surrounding areas; the present work adds to the understanding of the Bighorn Dolomite through subsurface well log and core analysis.

Subsurface observations from the Moxa Arch and vicinity

Subsurface log data from the Moxa Arch show the Bighorn Dolomite thinning from greater than 120 m on the northern tip of the Moxa Arch to 67 m near the Wyoming–Utah border (Fig. 4). The thinning is believed to be the result of post-Ordovician erosion (Sloss, 1963; Goodwin, 1964). The Bighorn Dolomite is absent within the Uinta Uplift, located

in northern Utah and Colorado at the southern tip of the Moxa Arch (Rowley et al., 1985), where the Mississippian Madison Limestone lies disconformably on Cambrian strata. Log interpretations suggest the Steamboat Point Member comprises most of the Bighorn in the subsurface, however up to 21 m of an overlying less massive member may also be present (most likely the Leigh Member).

Cores are rare through the Lower Paleozoic section, yet one partial core of the Steamboat Point Member was available for viewing from the northern Moxa Arch (see Fig. 1 for location). This core, nearly 100 percent dolostone, shows three distinct textures. The most common texture, comprising as much as 85 percent of the available core, is the characteristic mottled dolostone (Fig. 5A). This texture has been described in outcrops by numerous authors, and Zenger (1996) most recently attributed it to preferential early dolomitization of *Thalassinoides*-like burrows. The mottled texture involves noticeable porosity contrasts (over several centimeters). Relatively coarse-grained light tan dolostone has vuggy porosity, whereas vugs are rare in the fine-grained dark tan to brown dolostone. The second texture is similarly mottled but on a smaller scale (mottles less than one centimeter long) and is most likely also the result of preferential dolomitization of pre-existing burrows (Fig. 5B). This texture comprises approximately 5 percent of the core and may result in less of a porosity contrast because the light and dark texture (porosity) variations occur on scales less than 1 cm and are often interconnected. The third texture is a dolomitic mudstone (Fig. 5C) that is medium brown to gray

Figure 3. Photograph of Steamboat Point Member of Bighorn Dolomite taken in Sinks Canyon, in the Wind River Range, near Lander, Wyoming, approximately 150 km northeast of the Moxa Arch. The Steamboat Point Member (black arrow) is 50 m thick.
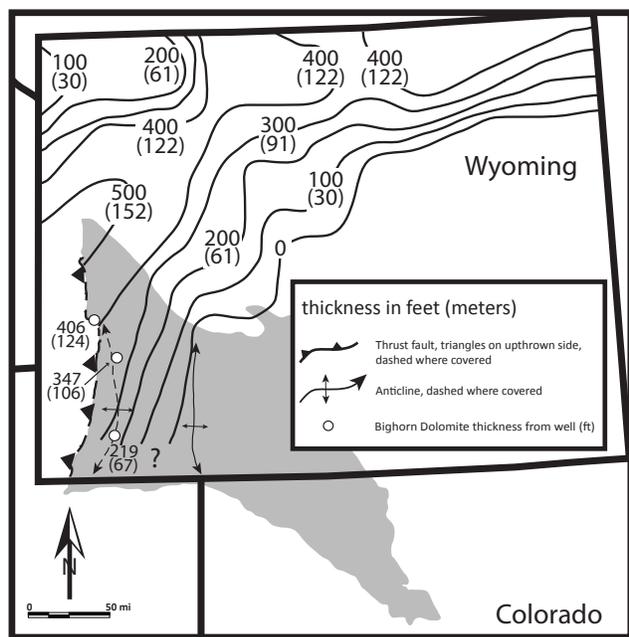
Figure 4. Isopach map of the Bighorn Dolomite in Wyoming. Circles indicate thickness of Bighorn Dolomite as interpreted from well logs; the Greater Green River Basin is highlighted in gray; the front of the Sevier fold-and-thrust belt, Moxa Arch, and Rock Springs Uplift are represented with map symbols (see Fig. 1). Modified from Peterson (1989).

and comprises 10 percent of the core. It commonly includes thin wispy stylolites that are not well developed and are discontinuous laterally through the core. This dolomitic mudstone does not display visible porosity and very rarely contain vugs.

Reservoir characteristics

Although only visual inspection of the Bighorn Dolomite core was possible, it is clear that porosity and permeability, essential reservoir qualities, are affected by heterogeneities at a range of scales. In hand sample, there are centimeter-scale porosity variations probably resulting from the dolomitization process and subsequent deformation. Compaction produced a complex network of mutually cross-cutting stylolites, and deformation and change in stress resulted in the formation of fractures. Preferential fluid pathways and baffles and barriers to flow were formed by these permeability variations, suggesting reservoir heterogeneity at a multitude of scales.

Heterogeneities within the Bighorn Dolomite can be subdivided into three categories: structural, compaction-related, and lithologic. Structural het-

erogeneities are fractures and faults (Fig. 6A), which can enhance or hinder fluid migration within a reservoir, depending on the nature of the structural heterogeneity and the type of fill. In the core, fracture apertures ranged from less than 0.1 to 0.5 mm, and the fractures were variably unfilled or filled with calcite. Compaction resulted in the formation of stylolites, which are pressure-solution seams along which rock is dissolved, leaving an insoluble residue at the interface. The residue can be an impermeable barrier and, in the case of Figure 6B, creates a visible break between higher and lower porosity zones. Lithologic heterogeneities include variations in texture (Fig. 5) and in composition, such as the difference between a low-porosity dolomite mudstone and a higher-porosity mottled dolostone. Lithologic heterogeneities may be the result of stratigraphic variation over tens to thousands of meters, and encompass various facies and lithologies that are preserved during basin filling or subsequent diagenesis. As documented regionally, all four members of the Bighorn Dolomite display lithologic heterogeneities with varying amounts of dolomitization within and between members and locations. Structural, compaction, and lithologic heterogeneities combine to create internal baffles within the Bighorn Dolomite, complicating its evaluation as a reservoir.

JEFFERSON FORMATION AS A SEAL

More difficult than identification of a potential porous and permeable reservoir unit in the subsurface is assessment of the effectiveness of an overlying low permeability sealing unit. The seal must both hold a buoyant column and be laterally continuous across the trap.

Devonian stratigraphy in southwest Wyoming

Devonian strata in the subsurface of southwestern Wyoming have been the subject of unresolved discussion for several decades, most likely due to the scarcity of subsurface data. The Devonian section in the subsurface of the Greater Green River Basin is referred to as the "Darby Formation," as coined by Blackwelder (1918). The type locality of the Darby Formation is disputed (Love, 1969), and the naming scheme for Devonian formations/members in the subsurface is not clear. Original work by Peale (1893)
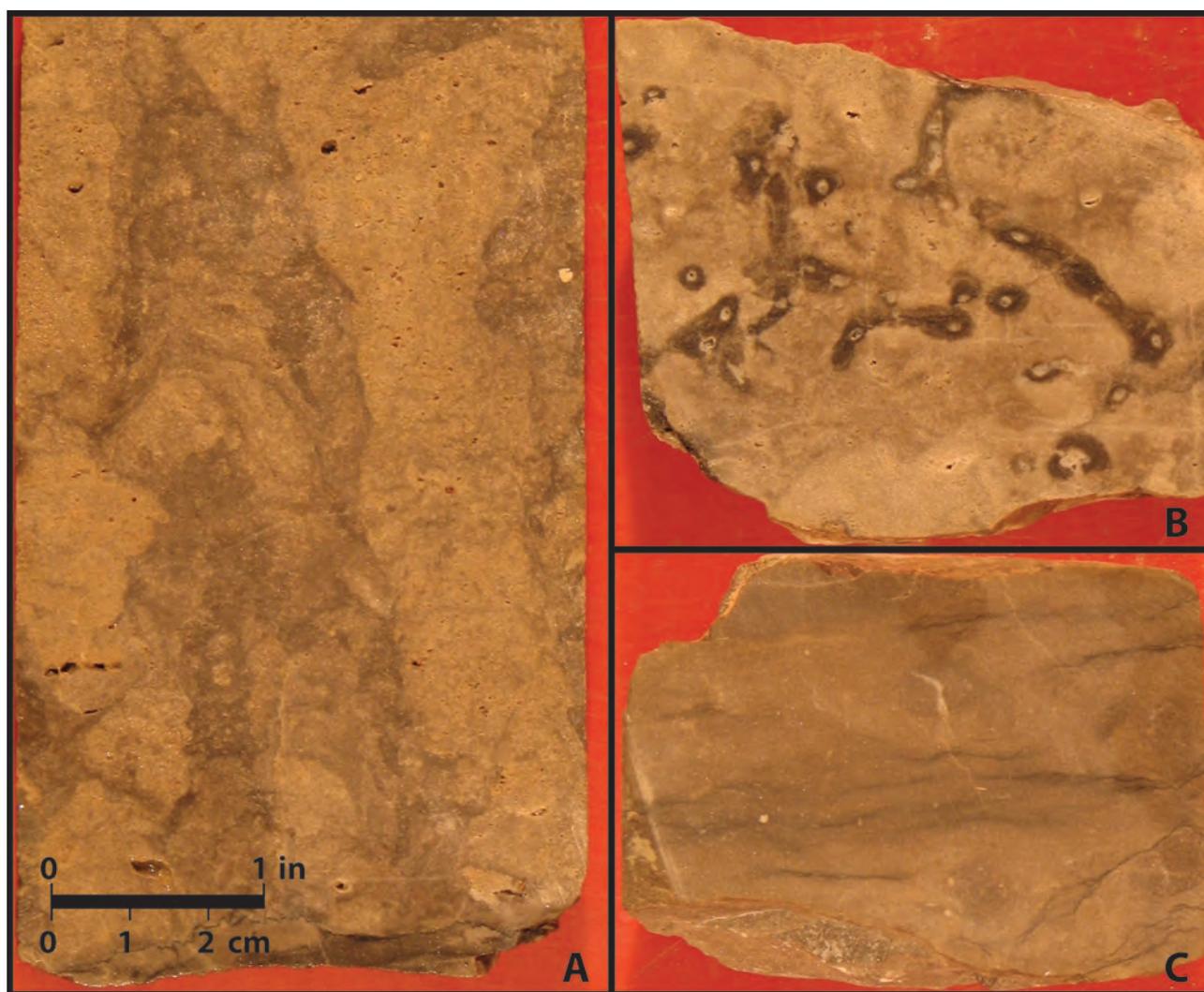
Figure 5. Textures observed in core (see Fig. 1 for location) from Steamboat Point Member of the Bighorn Dolomite. *A*, Mottled (bioturbated) dolostone. *B*, Small-scale mottled (bioturbated) dolostone. *C*, Dolomite mudstone.

subdivided the Devonian strata in southwestern Montana into the Jefferson Formation (lower) and the Three Forks Formation (upper). Subsequent studies proceeded to subdivide these formations into a variety of members based on studies at differing locations throughout Montana, Wyoming, Idaho, and Utah (e.g., Emmons and Calkins, 1913; Sandberg, 1962, 1965).

The most comprehensive study of the Devonian strata in western Wyoming was first published in a thesis by Benson (1965) and in his follow-up paper (Benson, 1966). Benson (1965, 1966) subdivided the Devonian section in western Wyoming into the Jefferson Formation and the overlying Three Forks Formation (Fig. 7). The Jefferson Formation

can further be subdivided into the unnamed Lower Member, which is a series of interbedded limestones, dolomites, evaporites, and clastics approximately 25 to 150 m thick, and the Birdbear Member, a distinctive massive and mottled buff-colored cliff-forming dolostone. Birdbear outcrops range in thickness from 18 to 35 m and are erosionally truncated along a north-south trend from the west side of the Big Horn Basin to the western Wind River Mountains and into the Green River Basin (Benson, 1966; Sandberg, 1965). Erosional truncation, evidence for subaerial exposure, and basal clastic beds in the Three Forks Formation (Benson, 1966) suggest sea level regression between deposition of the Jefferson Formation and the overlying Three Forks
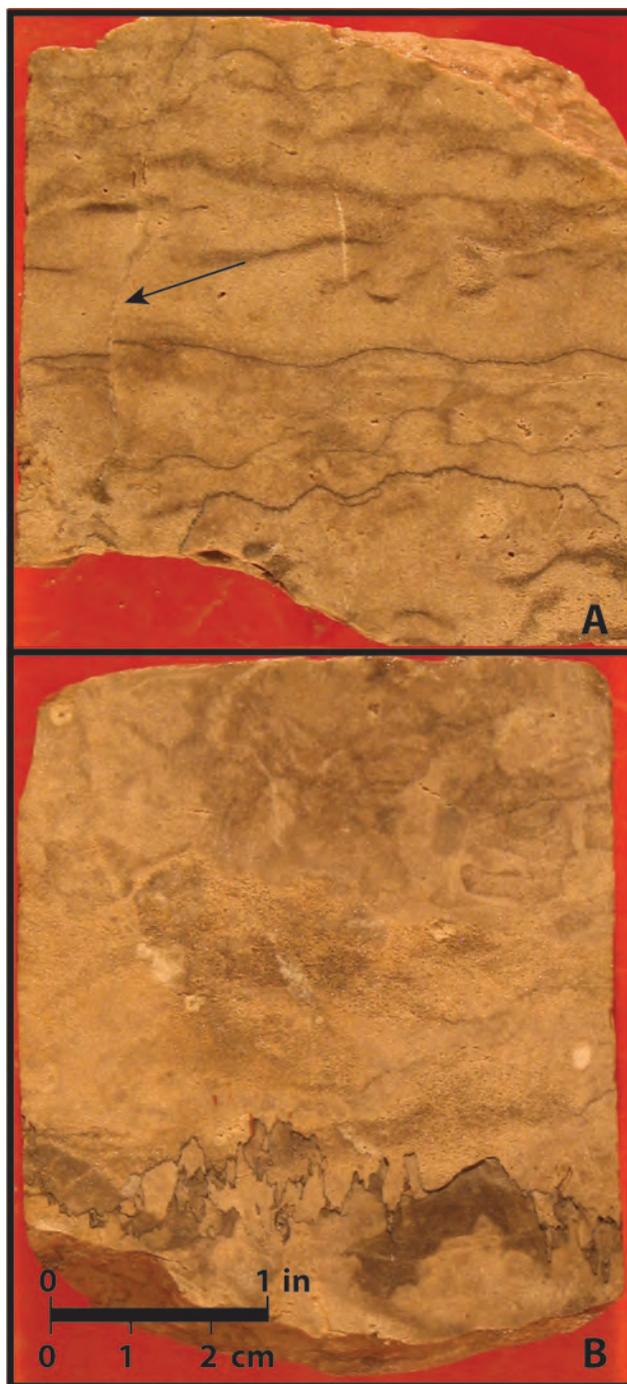
Figure 6. Bighorn Dolomite core photograph showing structural and compaction heterogeneities. *A*, Small calcite-filled fracture with mm-scale offset (arrow). *B*, Well-developed stylolite near base of core with high porosity zone above stylolite and low porosity below stylolite.

Formation. There are few constraints on the age of the Jefferson Formation. Laird (1947) used faunal correlation from Montana to Nevada to New York

to propose a Late Devonian age. Benson (1966) suggested the Jefferson Formation is Frasnian (385.3 to 374.5 Ma), and Johnson et al. (1985) used conodont zonal sequences to place most Jefferson deposition during the Frasnian. More recent work by Grader and Dehler (1999) and Grader et al. (2009) correlated Frasnian strata in east-central Idaho with the Jefferson Formation in eastern Idaho and southwestern Montana (Fig. 7).

The Three Forks Formation, which extends from Montana to east-central Idaho and western Wyoming, comprises thick (up to 30 m) evaporites and solution breccias interbedded with carbonates (limestones and dolostones) and shales (Rau, 1962; Benson, 1966). Several members have been described within the Three Forks Formation at various locations (i.e., Logan Gulch Member, Trident Member, Sappington Member, etc.). For simplicity, and because these members were defined far from western Wyoming and are difficult to correlate to the subsurface record, we use the term "Three Forks Formation" without distinguishing members. The Three Forks is generally considered Famennian from detailed stratigraphic correlations and ammonite zones (Gutschick et al., 1962; Sandberg, 1963, 1965).

The Jefferson and Three Forks Formations are overlain in places by what Sandberg (1963) termed the dark shale unit. The dark shale unit is dark gray carbonaceous marine shale and mudstone, interbedded with light brown silty dolomite (Benson, 1966). The unit is up to 25 m thick in northwestern Wyoming and contains conodonts of latest Devonian age (Sandberg and Klapper, 1967). The dark shale unit is interpreted as lying above a regional unconformity and is associated with deposition of the overlying Mississippian Madison Limestone.

As noted above, the term "Darby Formation" is commonly applied to the entire Devonian section. Benson (1966) correlated the Darby Formation with the Lower Member of the Jefferson Formation and suggested using "Darby Formation" only when the Birdbear Member of the Jefferson Formation and the Three Forks Formation are absent. Following this reasoning, we will not use the term "Darby Formation" for the subsurface Devonian strata in western Wyoming, because we consider the Birdbear Member and the Three Forks Formation to be recognizable there.
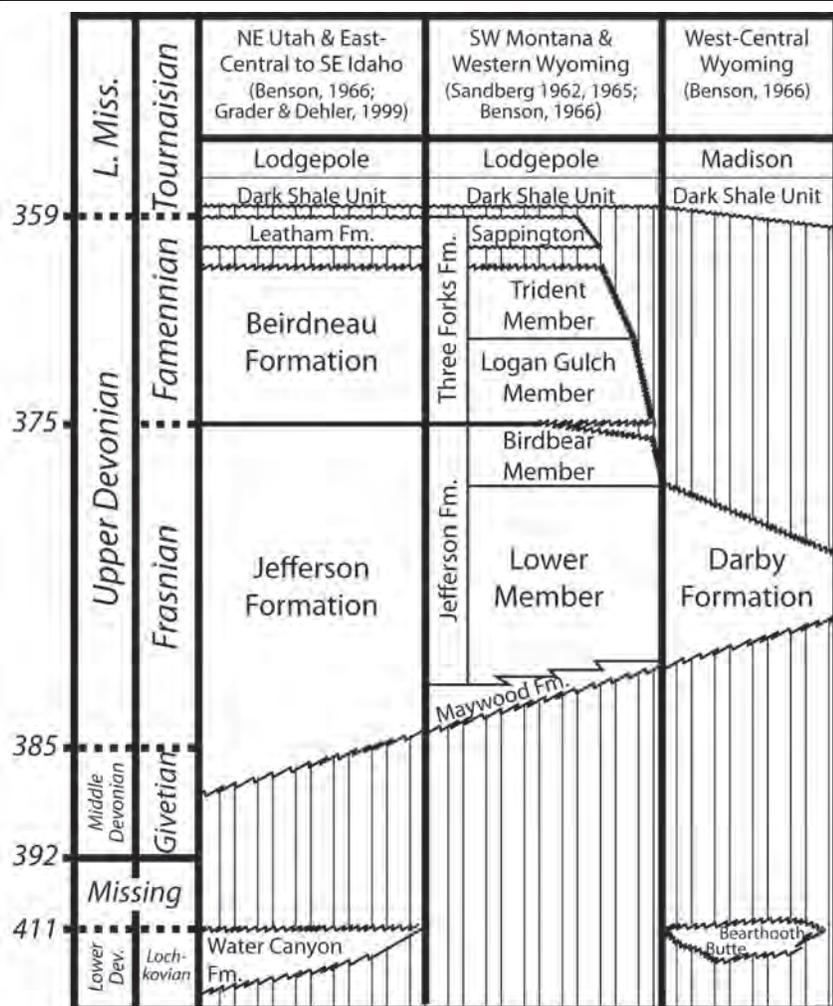
Figure 7. Devonian and Lower Mississippian stratigraphic terminology, modified from Benson (1966) with additions from Grader and Dehler (1999). Ages (Ma, at left) from the International Stratigraphic Chart (2009).

Surface and subsurface observations

We created a measured section for the interval between the Bighorn Dolomite and the Madison Limestone to understand better the log signature of the Devonian strata in the Greater Green River Basin. The most complete accessible section is on the northeast side of Fred's Mountain near Grand Targhee Ski Resort, Wyoming (base at longitude -110.9097 W, latitude 43.7839 N; Fig. 8).

At this location, the entire Devonian section is 100 m thick (Fig. 8). The Lower Member of the Jefferson Formation forms a slope with thin ledges 30 cm to 3 m thick. The ledges are resistant dark to medium brown, sucrosic-textured, thin-bedded dolostone, or light brown to gray brecciated dolostone and limestone. The brecciated units are interpreted as the result of evaporite solution collapse and have also been documented in east-central Idaho (Grader et al., 2009). Minor chert

nodules and vugs are present, as are rare recognizable gastropods, echinoderm plates, and peloids. Interbedded with the dolostones and minor limestones are thin (30 cm or less) beds of non-resistant detrital siliclastic sandstone, siltstone, and claystone. These beds are primarily composed of very fine-grained to fine-grained, well-rounded and well-sorted, frosted quartz grains. The detrital beds are recessive and poorly exposed on the slope of the Lower Member. There is a 3.4-m-thick dolomitized bioturbated wackestone in the upper quarter of the Lower Member of the Jefferson Formation. Most of the Birdbear Member forms a covered slope, but the top 6 m is a resistant, massive, and heavily bioturbated cliff-forming dolostone. The Three Forks Formation is entirely covered at this location. The overlying 3-m-thick dark shale unit is recognizable by its dark gray color and distinctive *Zoophycos* trace fossils.

To complement the outcrop study, we were able to locate (at the United States Geological Survey (USGS) Core Research Center in Lakewood, Colorado) Devonian cuttings from four wells on the Moxa Arch and one complete Devonian core from the Rock Springs Uplift, 40 km east of the Moxa Arch. Analysis of the cuttings indicate that the primary lithologies include dolostone, limestone, sandstone, siltstone, claystone, and occasional coal fragments, micas, and pyrite. Textures are not apparent from the cuttings. The core is from the 4-UPRR-11-19-104 well (longitude -109.105 W, latitude 41.64011 N; Fig. 9), and the Devonian section in
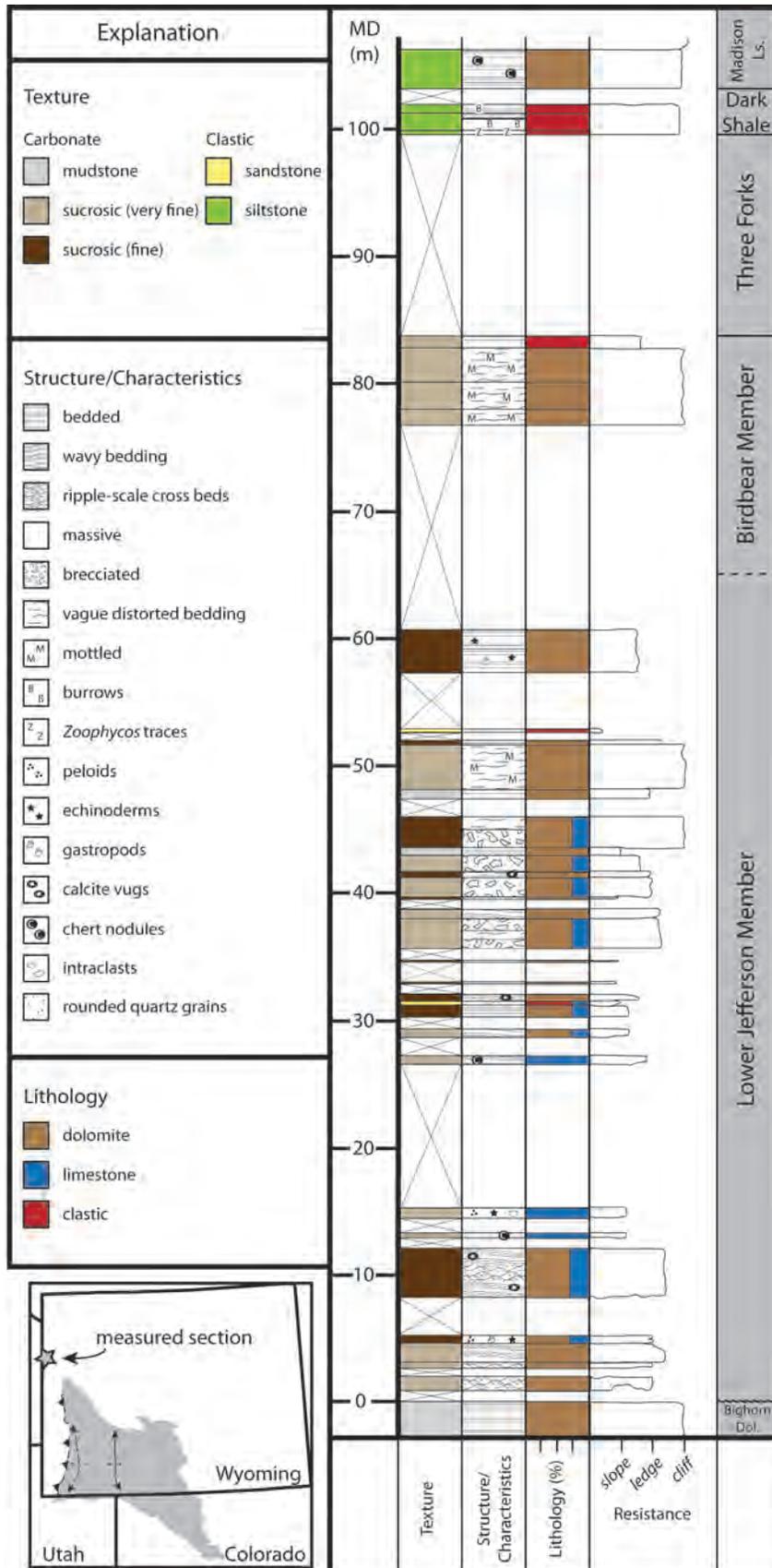
Figure 8. Measured section through the Jefferson and Three Forks Formations, measured at outcrops in northwest Wyoming near Grand Targhee Ski Resort (base at longitude -110.9097 W, latitude 43.7839 N).

this core is 37 m thick (Fig. 9). The 4-UPRR-11-19-104 core is interesting because the primary lithology is sandstone with very fine-grained to medium-grained, well-rounded and well-sorted, frosted quartz grains that are distributed fairly evenly throughout the core. In addition, there are two brecciated intervals located midway and at the top of the core, suggesting possible surface exposure. The Devonian in this core has been called the Darby Formation, but as previously mentioned we will assign it to the Lower Member of the Jefferson Formation.

Correlating the Devonian strata in the subsurface is challenging. Only a few wells have been logged in the Devonian in the Greater Green River Basin, and there are no marker log signatures, because the detrital material, argillaceous mudstones, and carbonates of the Lower Jefferson Formation are interbedded over centimeters to meters. Furthermore, since detailed age control is not available in the subsurface, interpreting the Lower Jefferson Formation in a sequence stratigraphic context is nearly impossible.

Figure 10 is a north–south cross section along the crest of the Moxa Arch of the complete Devonian section. Lithologic correlation of the Lower Jefferson interval points to a recurring series of anhydrite beds, as evidenced by low gamma and high density
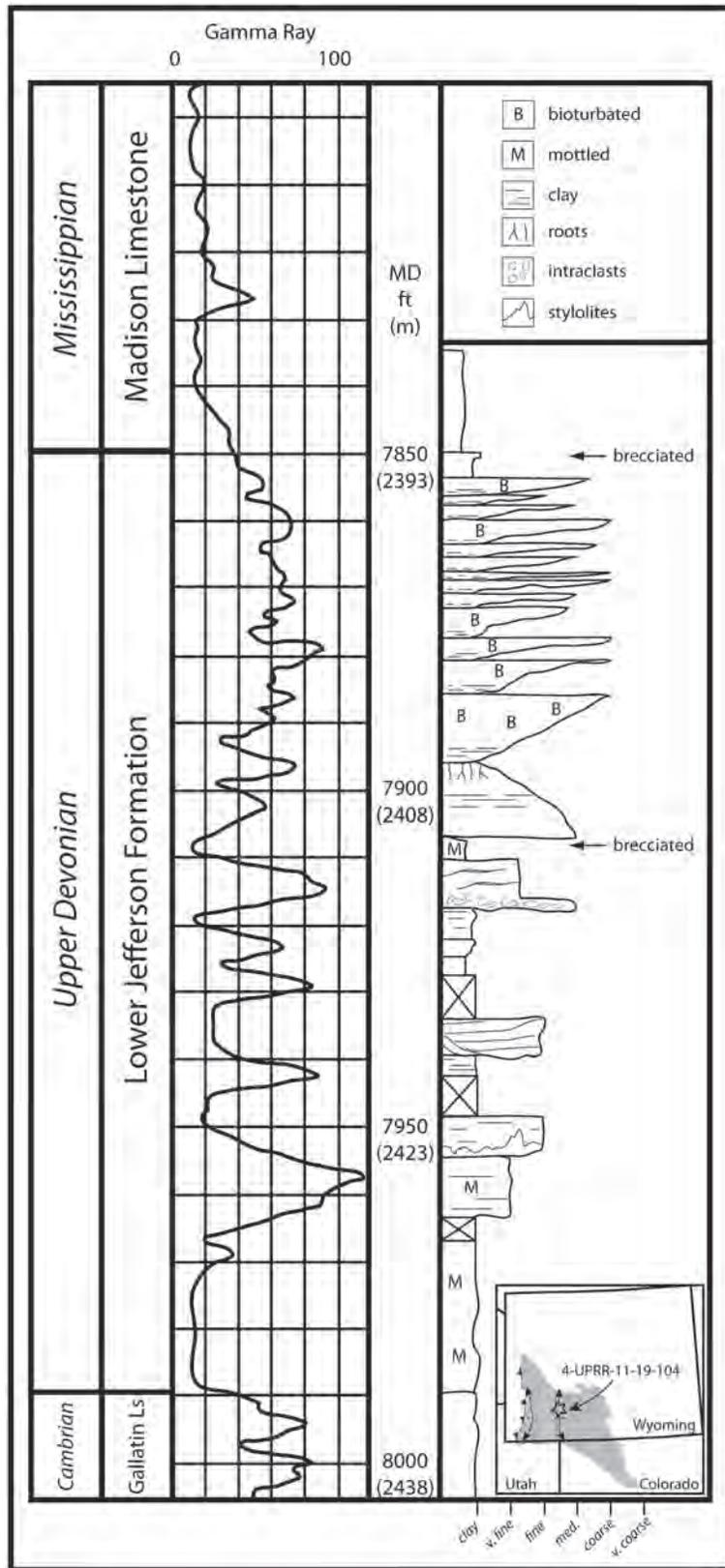
Figure 9. Lower Member of the Jefferson Formation core correlated with gamma ray log from the 4-UPRR-11-19-104 well, located on the Rock Springs Uplift (see inset map). Birdbear Member of Jefferson Formation and Three Forks were removed by pre-Mississippian erosion. A clastic horizontal scale was chosen for the core description because of the profusion of well-rounded quartz grains.

signatures. Although log correlation suggests some of these anhydrites may be continuous between wells, their minimal thickness (0.3 to 1.2 m) allows other interpretations. These anhydrite layers are significant because anhydrite may be the most common reservoir seal worldwide (Hangx et al., 2010).

Anhydrite Sr isotopic analysis

To determine if the anhydrite zones could be correlated from well to well, we identified several thin anhydrite beds from the logs and sampled anhydrite from Lower Jefferson Formation well cuttings (see Fig. 1 for geographic location of wells). Our intent was to use $^{87}Sr/^{86}Sr$ isotopic ratios as a possible correlation tool. If the anhydrite crystallized on broad and shallow tidal flats from the evaporation of seawater, then the $^{87}Sr/^{86}Sr$ ratio of anhydrite from equivalent stratigraphic levels should be identical. In addition, the Sr isotopic ratio should follow the Frasnian (385.3 to 374.5 Ma) seawater curve (e.g., Denison et al., 1997), which is not static throughout Frasnian time.

Laboratory methods

Anhydrite cuttings, averaged over a 10-ft (3-m) interval, were handpicked from cuttings stored at the USGS Core Research Center and dissolved in ultra-pure
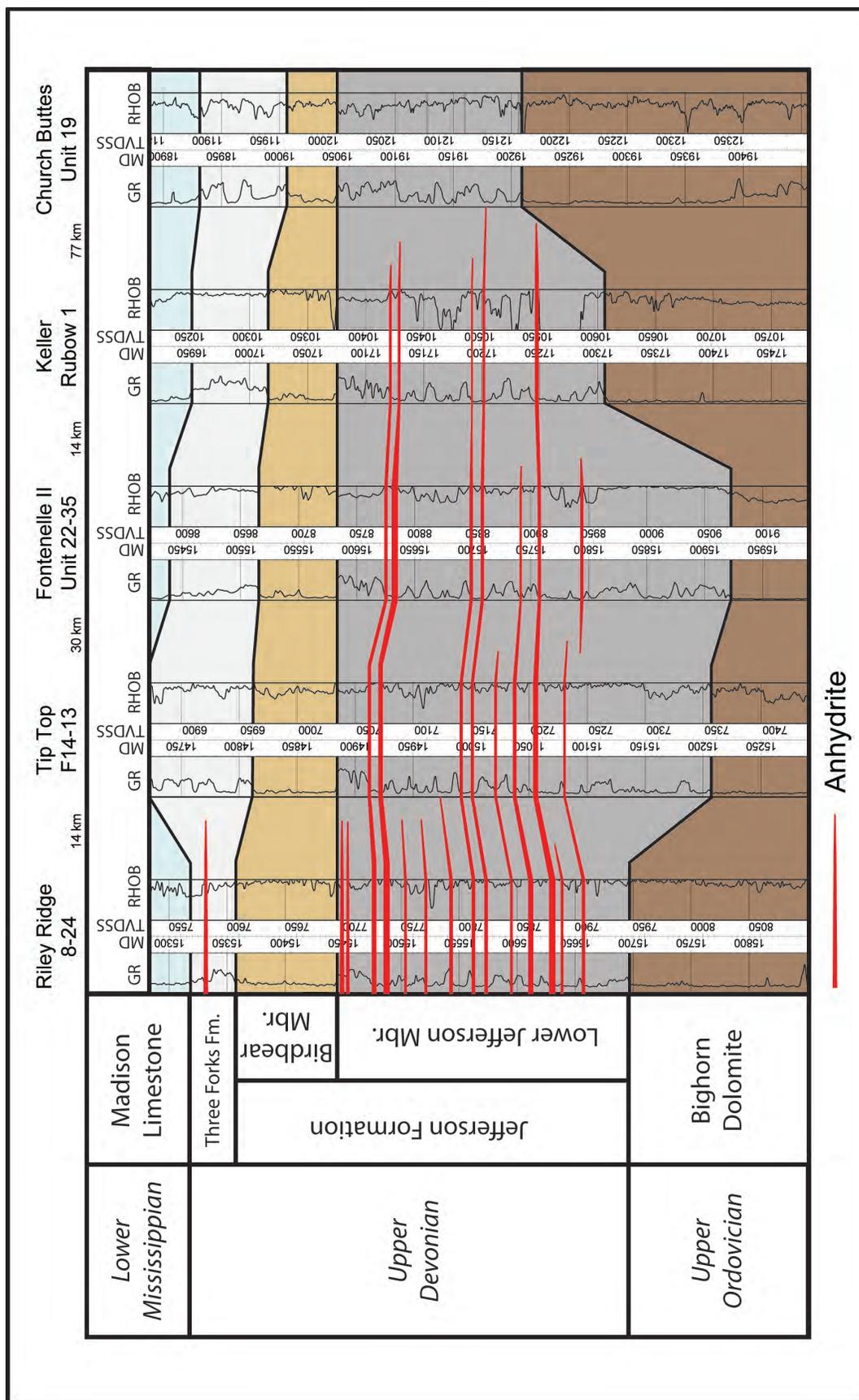
Figure 10. Correlation of Devonian section in five wells from north to south on the Moxa Arch (see Fig. 1 for locations). Red indicates anhydrite layers, depths are measured in feet, and log values increase to the right. Note the datum is a lithostratigraphic correlation at the base of the Birdbear Member.

water. One ml of solute was dried and redissolved in dilute nitric acid. Strontium was isolated using Teflon columns filled with Eichrom® Sr-Spec resin. The strontium isotopic composition was determined by thermal ionization mass spectrometry at the University of Wyoming. All analyses were normalized to an $^{86}Sr/^{88}Sr$ ratio value of 0.1194. Analytical blanks are less than 0.2 ng Sr. Six analyses of NBS 987 strontium standard measured during the course of these analyses gave an average value of $^{87}Sr/^{86}Sr$ = 0.71026 ± 0.00002 (2 standard deviations), identical to a long-term average of 0.71026 ± 0.00002 (2 standard deviations) based upon 76 analyses of the standard. Values are reported relative to modern seawater, defined as:

$$\Delta_{sw} = (^{87}Sr/^{86}Sr_{sample} - ^{87}Sr/^{86}Sr_{modern\ seawater}) \times 10^5 \qquad (1)$$

where the $^{87}Sr/^{86}Sr$ of modern seawater is taken to be 0.709173 (McArthur, 1995).

Sr isotopic results

Sr isotopic results for 29 samples of anhydrite are reported on Table 1. Twenty-seven samples were taken from the Graphite 116, Fontanelle II Unit 22-35, Keller Rubow 1, and Church Buttes Unit 19 wells on the Moxa Arch (see Fig. 1 for location). Two additional samples, interpreted as secondary anhydrite that fills fractures, are from the 4-UPRR-11-19-104 core on the Rock Springs Uplift to the east (see Fig. 9 for location). Sr isotopic composition of most samples from the Moxa Arch wells are between $^{87}Sr/^{86}Sr$ of 0.70822 and 0.70905 (Δ_{sw} = -69.3 to -12.3), but three are higher, ranging from 0.70931 to 0.71081 (Δ_{sw} = 13.4 to 164.2). Both samples from the Rock Springs Uplift are among the most radiogenic: 0.70982 and 0.71083 (Δ_{sw} = 64.3 and 165.3). All are higher than the estimates for contemporary Frasnian seawater (0.70795 to 0.70815; Denison et al., 1997; John et al., 2008).

Sr isotopic data discussion

All Sr isotopic ratios for our anhydrite samples are more radiogenic than Frasnian seawater values. This suggests that if the anhydrite is primary, it was not formed in an open marine environment, but instead was precipitated from a water body that was partially or totally isolated from the ocean. Denison et al. (1998) applied the term salina to such a body of water, which can be dominated by marine water, by continental runoff, or a combination of the two. If

Table 1. Sr isotopic data for anhydrite from well cuttings of Devonian rocks from the Moxa Arch and Rock Springs Uplift.

Top Depth (ft)	$^{87}Sr/^{86}Sr$	internal precision (% std. error)	Δ_{SW}
Keller Rubow 1			
17200	0.70848	0.0017	-69.27
17220	0.70845	0.0015	-72.03
17230	0.70877	0.0013	-39.87
17250	0.70823	0.0016	-94.61
17260	0.70861	0.0014	-56.57
17270	0.70879	0.0015	-38.44
17280	0.70931	0.0016	13.44
17290	0.71081	0.0014	164.18
17300	0.70882	0.0017	-35.52
Graphite 116			
17260	0.70868	0.0019	-49.32
17270	0.70855	0.0017	-61.85
17280	0.70905	0.0016	-12.3
17290	0.70863	0.0016	-54.69
Fontanelle II Unit 22-35			
15680	0.70874	0.0038	-43.01
15690	0.70815	0.0016	-102.54
15710	0.70856	0.0016	-61.47
15720	0.70943	0.0020	25.24
15730	0.70814	0.0014	-102.91
15740	0.70869	0.0016	-48.79
15760	0.70869	0.0026	-48.46
15770	0.70857	0.0017	-60.21
15780	0.71078	0.0014	160.85
15790	0.70839	0.0016	-78.55
15800	0.70852	0.0016	-65.23
15810	0.70841	0.0017	-76.24
15820	0.70880	0.0017	-37.65
Church Buttes 19			
19180	0.70868	0.0029	-49.79
4-UPRR-11-19-104			
7902	0.71083	0.0016	165.26
7921	0.70982	0.0013	64.27

Note: See Fig. 1 for Moxa Arch and Rock Springs Uplift locations. All depths are in measured depth.

the $^{87}Sr/^{86}Sr$ ratio and Sr concentration of the seawater and the continental runoff are known, then the mass

balance of a mixture of marine and continental water may be determined. The Sr isotopic composition of seawater has been determined from analyses of marine carbonates and, as noted above, the Frasnian seawater values varied from 0.70795 (Δ_{sw} of -122) in Early Frasnian, to a high of 0.70815 (Δ_{sw} of -102) in Middle Frasnian. The concentration of Sr in seawater is approximately 8 ppm, much greater than in average river water (~60 ppb; Denison et al., 1998). Modern major river water has Δ_{sw} of 100 to 300 (Palmer and Edmond, 1992). However, the isotopic ratio and Sr concentration of individual rivers varies widely and are very much dependent upon the geology and geography of the drainage basin. Thus we do not know with any certainty the Sr isotopic composition and Sr concentration of the rivers that may have supplied a Devonian salina in present-day western Wyoming. A widespread unconformity at the base of the Paleozoic section in the Uinta Mountains, Wind River Range, and throughout the Laramide uplifts of Wyoming suggests that Precambrian rocks were a source for terrigenous input. Exposed Cambro-Ordovician carbonates are another potential source of non-marine Sr to the Late Devonian salinas. As a result, we can make only general estimates of the proportions of marine and meteoric water in the water body from which the anhydrite precipitated.

For the purpose of illustration we calculate the fraction of marine water in the salina using three different estimates of the $^{87}Sr/^{86}Sr$ ratio of the continental end member: one based upon modern rivers draining Paleozoic and older rocks on the margins of the Greater Green River Basin, a second estimate based upon modern average river Sr isotopic composition, and a third using the radiogenic $^{87}Sr/^{86}Sr$ ratios of the secondary anhydrite derived from the 4-UPRR-11-19-104 to approximate the continental end member. These three approaches give overlapping estimates of the $^{87}Sr/^{86}Sr$ ratio for Devonian continental runoff in the vicinity of the present-day Green River Basin. First, modern water sampled in the Greater Green River Basin near the headwaters of the Green, Big Sandy, and Sweetwater Rivers where they have traversed mainly Archean and Paleozoic rocks have $^{87}Sr/^{86}Sr$ ratios of 0.7212 to 0.7157 (Fenner and Frost, unpublished data). Assuming these rocks also supplied Sr to meteoric water in Frasnian time and correcting for radiogenic ingrowth of ^{87}Sr by the decay of ^{87}Rb in the rocks since Frasnian time, the Δ_{sw} of Devonian mete-

oric water may have been around 100 to 400. Second, for modern rivers, mean Δ_{sw} is estimated at 100 to 300. Third, if the fluids from which the secondary anhydrite in the 4-UPRR-11-19-104 core (Rock Springs Uplift) precipitated represent an estimate of local continental meteoric water (Δ_{sw} of 64 to 165), then those Sr isotopic ratios may also be reasonable estimates of the continental end member. Accordingly, we performed mixing calculations using continental end members Δ_{sw} of 100, 300, and 400.

We used two different estimates of Sr concentration of continental runoff (60 ppb and 300 ppb) to represent the mean Sr concentrations of 60 ppb of modern rivers and a higher Sr content typical of arid river water (Denison et al., 1998). The results of the calculations are displayed in Table 2. The calculations were done using the two-component mixing model of Faure (1986). These calculations suggest that if the concentration of Sr in the continental water was 60 ppb, then the water body from which the anhydrite precipitated was dominated by the continental component; the fraction of marine water is less than 10 percent for all but the three anhydrites with the lowest Sr isotopic compositions, which are closest to contemporary seawater values. If the concentration of Sr in the continental end member was higher (300 ppb), then the proportion of marine water is higher, up to 36 percent for most samples and higher for the three anhydrite samples with the lowest Δ_{sw} (Fig. 11). If these anhydrites are secondary, then they precipitated from a different fluid than one that produced the higher ratio group.

The three samples from the Moxa Arch wells with higher Δ_{sw} and the two Rock Springs Uplift samples that are clearly secondary fracture fills precipitated from fluids with Sr isotopic characteristics expected of continental meteoric waters. It is possible that the three Moxa Arch samples are primary precipitates that formed when the salina was supplied entirely by continental runoff, or they could be secondary. In either case, the depositional environment was not entirely marine and exhibits a strong contribution of meteoric water, probably sourced from the adjacent continent.

Seal characteristics

Lithology alone indicates that depositional environments of the Jefferson Formation include marine (carbonates), marginal marine (carbonates, evapo-

Table 2. Mass balance calculations of proportions of seawater and continental runoff in Frasnian (Upper Devonian) salinas.

Top Depth (ft)	Anhydrite Δ_{SW}	fraction marine for various river Δ_{SW}, 60 ppb Sr			fraction marine for various river Δ_{SW}, 300 ppb Sr		
		$\Delta_{SW}=$ 100	$\Delta_{SW}=$ 300	$\Delta_{SW}=$ 400	$\Delta_{SW}=$ 100	$\Delta_{SW}=$ 300	$\Delta_{SW}=$ 400
Keller Rubow 1							
17200	-69.3	0.03	0.06	0.08	0.13	0.25	0.30
17220	-72.0	0.03	0.07	0.09	0.15	0.27	0.32
17230	-39.9	0.01	0.04	0.04	0.07	0.15	0.19
17250	-94.6	0.09	0.16	0.19	0.32	0.49	0.55
17260	-56.6	0.02	0.05	0.06	0.10	0.20	0.24
17270	-38.4	0.01	0.03	0.04	0.07	0.15	0.19
17280	13.4	0.01	0.02	0.02	0.03	0.08	0.11
17290	164.2	0.00	0.00	0.01	-0.01	0.02	0.03
17300	-35.5	0.01	0.03	0.04	0.06	0.14	0.18
Graphite 116							
17260	-49.3	0.02	0.04	0.05	0.08	0.18	0.22
17270	-61.9	0.02	0.05	0.07	0.11	0.22	0.26
17280	-12.3	0.01	0.02	0.03	0.04	0.11	0.14
17290	-54.7	0.02	0.05	0.06	0.09	0.19	0.24
Fontanelle II Unit 22-35							
15680	-43.0	0.02	0.04	0.05	0.07	0.16	0.20
15690	-102.5	0.17	0.29	0.34	0.50	0.67	0.72
15710	-61.5	0.02	0.05	0.07	0.11	0.22	0.26
15720	25.2	0.00	0.02	0.02	0.02	0.07	0.09
15730	-102.9	0.18	0.30	0.35	0.52	0.68	0.73
15740	-48.8	0.02	0.04	0.05	0.08	0.18	0.22
15760	-48.5	0.02	0.04	0.05	0.08	0.18	0.21
15770	-60.2	0.02	0.05	0.06	0.11	0.21	0.26
15780	160.8	0.00	0.00	0.01	-0.01	0.02	0.03
15790	-78.6	0.04	0.08	0.10	0.18	0.31	0.36
15800	-65.2	0.03	0.06	0.07	0.12	0.23	0.28
15810	-76.2	0.04	0.08	0.10	0.16	0.29	0.35
15820	-37.7	0.01	0.03	0.04	0.07	0.15	0.18
Church Buttes 19							
19180	-49.8	0.02	0.04	0.05	0.09	0.18	0.12
4-UPRR-11-19-104							
7902	165.3	0.00	0.00	0.01	-0.01	0.02	0.12
7921	64.3	0.00	0.01	0.01	0.01	0.05	0.12

Note: For all calculations, the Δ_{SW} and Sr concentration of Frasnian seawater is assumed to be -110 and 8 ppm, respectively. All depths are in measured depth.
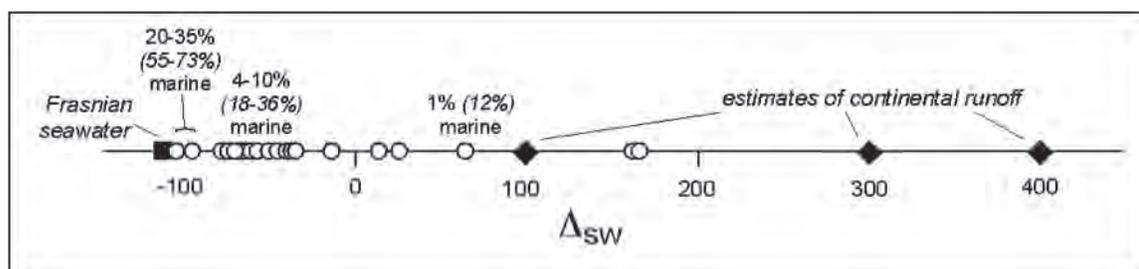
Figure 11. Number line plotting the Δ_{sw} of the end member seawater and three estimates of continental runoff used in binary mixing calculations (solid diamond symbols) and the Δ_{sw} of analyzed Frasnian anhydrite samples (open circle symbols). The maximum calculated percentage of the marine component, which is obtained using the most radiogenic Δ_{sw} of 400, is given for selected groups of anhydrite samples. The percentages in regular font are based on a continental Sr concentration of 60 ppb and the percentages in italics are based on a continental Sr concentration of 300 ppb. Because seawater has much higher Sr concentration than continental runoff, a small proportion of marine water in the salina yields mixtures with Δ_{sw} only slightly higher than the seawater value. Data from Table 2.

rites, clastics), and perhaps even periods of subaerial exposure (evaporites, breccias). The 4-UPRR-11-19-104 core from the Rock Springs Uplift (Fig. 9) is interpreted as a shallowing-upward sequence capped by a series of 14 peritidal coarsening-upward units. The abundance of cross-bedding with well-rounded and frosted quartz grains implies that this core represents parts of the Lower Jefferson Formation that were proximal to the source. Similar frosted grains are described in Upper Devonian sections as far away as east-central Idaho (Grader and Dehler, 1999) and southeast Idaho (Beus, 1968). If these grains were eolian in origin (marine quartz overgrowth is a second interpretation), then either large regional sandstorms carried sediment far into the basin, nearshore dunes migrated with the shoreline during sea level fluctuations, or eolian material was reworked by rivers and tides. The relatively rare occurrence of clastic units in our measured section and in Benson's (1966) description from outcrops farther west (Idaho and Montana) suggests that western Wyoming and eastern Idaho are more distal (west) to the source than the preserved 4-UPRR-11-19-104 core on the Rock Springs Uplift (east).

We know from limited well logs and well cuttings from the Moxa Arch that thin anhydrite layers of questionable continuity are present. The anhydrite is interbedded within a series of thin dolostones, mudstones, and siltstones. These most likely reflect intertidal to possibly supratidal depositional environments, occasionally interrupted by carbonate deposition during shallow flooding. Results from Sr isotopic analysis indicate that anhydrite precipitated from a mixture of marine and continental waters, which leads us to conclude that the Lower Jefferson Formation in western Wyoming records the approximate position of the Frasnian shoreline. The coastal area was presumably broad with a very gentle slope toward the shelf and basin farther west.

The Sr isotopic ratios are not perfectly uniform either from well to well or vertically within wells. This suggests that the anhydrite layers did not form from a single, well-mixed water body. Perhaps there were several evaporative salinas that were spatially and temporally distinct. In this case, the waters in the salinas did not mix but contained water of similar Sr isotopic composition.

Alternatively, and perhaps more likely, the anhydrites at any one stratigraphic level may have been continuous. In this possibility, the salina would have received slightly varying amounts of meteoric water over time. We prefer this option because it is supported by well log interpretations. Logs from five wells on the Moxa Arch suggest a minimum of 130 km of correlatable dolostone and detrital units (Fig. 10). The anhydrites correlate over a maximum 60 km, as constrained by the few available well logs. This interpretation fits well with a broad shallow coastal area and high tidal influence (as noted in the 4-UPRR-11-19-104 core farther east).

We know independently from CO_2 concentrations on the Moxa Arch that the Jefferson and/or Three Forks Formations must seal the underlying Bighorn Dolomite reservoir from the overlying Madison Limestone. Our task, then, is to understand what makes the Devonian formations a successful seal.

Hangx et al. (2010) studied the mechanical behavior of anhydrite as a seal and found CO_2 penetration rates of approximately 3 m per 10,000 years. With this penetration rate, we must assume that the anhydrites in the Lower Jefferson Formation are far thicker than what can be determined from a gamma ray or neutron density log, and the combined effect of numerous thin but stacked anhydrite layers interbedded with lime mudstones and thin shales can seal a reservoir, or the evaporites in the overlying Three Forks Formation significantly contribute to the overall Devonian seal.

Based on one unpublished image log from the Jefferson Formation on the northern Moxa Arch and the amount of anhydrite recovered from cuttings where anhydrite was not interpreted from the density log signature, we believe there may be more and/or thicker anhydrite layers than originally noted. This stacked succession of laterally continuous (on the order of 50 to 100 km) evaporites may be the seal to the Bighorn Dolomite CO_2 reservoir.

CONCLUSIONS

Potential sites for long-term geologic storage of carbon dioxide should have a well-defined and well-understood trap, reservoir, and seal. The Lower Paleozoic rocks in the western Greater Green River Basin provide a natural CO_2 storage area because they possess all three attributes. The trap, the Moxa Arch, is a gently folded, doubly plunging anticline. The reservoir (Steamboat Point Member of the Upper Ordovician Bighorn Dolomite) has adequate porosity and permeability to hold large amounts of naturally occurring CO_2. The Lower Member of the Upper Devonian Jefferson Formation, perhaps in combination with the overlying Three Forks Formation, seals the CO_2 from the overlying Mississippian Madison Limestone.

Sr isotopic analyses of the anhydrite layers within the Jefferson Formation yield $^{87}Sr/^{86}Sr$ ratios mainly between 0.70822 and 0.70905, suggesting anhydrite formed in a salina environment and recorded a mixed seawater and meteoric water signature. This isotopic composition implies that, at least in the part of the section in which anhydrites are present, the Lower Jefferson Formation records the Frasnian paleo-shoreline. A few higher Sr isotopic ratios from wells on the Moxa Arch and from farther away on the Rock Springs Uplift most likely identify secondary fracture fills precipitated from a more radiogenic fluid. Based on log interpretations and $^{87}Sr/^{86}Sr$ ratios, we interpret that the anhydrite layers noted in the few deep wells on the Moxa Arch are continuous on scales up to 100 km. These stacked and continuous anhydrite layers in the Lower Member of the Jefferson Formation probably form the CO_2 seal between the Bighorn Dolomite and Madison Limestone.

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