# Lateral periodic variations in the petrophysical and geochemical properties of dolomite

David A. Budd,\* Matthew J. Pranter, Zulfiquar A. Reza

Department of Geological Sciences, University of Colorado, Boulder, Colorado 80309-0399, USA

### ABSTRACT

Mississippian dolowackestones contain periodic oscillations in the lateral distribution of trace-element concentrations, porosity, and permeability. Random variations at  $\leq$ 30 cm spacing account for 50%–70% of the total variability. The remainder of the variability occurs in short- and long-range oscillatory patterns with periods of 1.2–7.6 m, which can only be resolved by high-resolution sampling of an ~150 m lateral transect. Possible origins for these patterns are: (1) inheritance from the depositional precursor, (2) formation by self-organizing processes during dolomitization, or (3) overprinting by late diagenesis. These oscillatory patterns have up to now been unrecognized, and addressing their origin and meaning(s) represents a new approach to the study of dolomites. Understanding the lateral distribution of petrophysical properties can also improve models of fluid flow in dolomite aquifers. Further, if 30%–50% of the variability in a geochemical attribute in any bed is due to lateral periodicity, one must ask if that variability is too great to assume a spot sample will be a suitable proxy for ancient geologic processes and conditions.

Keywords: dolomite, trace elements, porosity, permeability, diagenesis, self-organization.

# INTRODUCTION

Dolomite rocks have been intensely researched for decades due to their importance as repositories of earth history and economic resources. In such studies, analysis commonly involves "representative" samples collected from vertical sections. Laterally, samples are typically dispersed at scales of  $10^2$  to  $10^5$  m, reflecting the spacing between measured vertical sections and/or subsurface cores. This type of sampling defines different genetic populations of dolomite and their stratigraphic and regional trends, but prevents lateral characterization of dolomite attributes at the scale of  $10^0$  to  $10^2$  m. The information that such data can convey about the processes of dolomitization, variance in geochemical records, or distribution of petrophysical properties is unknown.

Prior work on the lateral attributes of dolomites involved permeability studies in dolograinstones of the Permian San Andres Formation, southeast New Mexico, USA (Kerans et al., 1994; Eisenburg et al., 1994; Grant et al., 1994; Jennings, 2000). Permeability was measured at 30 cm intervals over lateral distances of 73–835 m. The results reveal multiple scales of lateral variability in permeability, including a near-random component at and below the 30 cm sampling interval, which accounts for 50%–60% of the total variance, and short- and long-range oscillatory patterns at 6–45 m, which account for the rest of the total variance.

To determine if the lateral oscillations in petrophysical properties observed in the San Andres Formation are present in other dolomite bodies, and to assess if there is periodicity in the geochemical properties of dolomites, we sampled an ~150 m lateral traverse in a single 6-m-thick dolowackestone bed of the Mississippian Madison Formation at Sheep Canyon, Wyoming (44°36′45″N, 108°8′10″W). The results show that lateral periodic oscillations in petrophysical and geochemical properties do exist in this Madison dolomite, which suggests that this may be a previously unrecognized characteristic of many dolomites.

# SETTING

Sonnenfeld (1996) defined six third-order stratigraphic sequences within the Madison (sequences I through VI; oldest to youngest, respectively). The bioturbated, skeletal dolowackestone sampled at Sheep Canyon is from the transgressive systems tract of sequence I, and was deposited in a middle ramp setting (Sonnenfeld, 1996). It is one of the most porous rock fabrics exposed at Sheep Canyon (Sonnenfeld, 1996; Smith et al., 2004). Early dolomitization of sequence I by refluxing evaporated seawater is interpreted to have occurred during the deposition of the upper Madison Formation (Crocket, 1994; Sonnenfeld, 1996; Moore, 2001), and slightly negative oxygen isotopic data indicate that some degree of recrystallization occurred during burial (Moore, 2001; Smith et al., 2004).

#### **METHODS**

Core plugs, 2.5 cm in diameter and 5–8 cm long, were obtained with a water-lubricated core drill at 30 cm intervals along the outcrop face. The outer 1–2 cm of each sample were trimmed off to avoid weathering effects, and a portion of the remaining material was trimmed to a length of 2.5–3.8 cm. Permeability measurements were made on ends of the trimmed cylinders using mini-probe permeametry (MPP). MPP measures gas flow rates through the sample, and those flow rates are converted to permeability based on empir-



Figure 1. Porosity, permeability, Sr, Na, Mn, and Fe versus distance in 147.3 m lateral transect through dolowackestone of Madison Formation. Solid lines are five-point moving averages.

<sup>\*</sup>E-mail: budd@colorado.edu.

ical calibration curves derived from a set of standards with known permeabilities (see Budd, 2001, for details). MPP analyzes millimeter-scale spots, so the reported permeability of each Madison sample is the geometric mean of four spot measurements, two from each end of the cylinder. Based on multiple analyses of the standards, the MPP has a precision of  $\pm 15\%$ . Porosity of the entire cylinder was measured with a reproducibility of 0.2% using a bulk-density technique.

For geochemical analyses, a subsample of each drill plug was ground to a fine powder and then examined by X-ray diffraction to determine if calcite was present. Powders that contained calcite were treated with a pHbuffered EDTA solution to remove the calcite. After treatment, each sample was rinsed and centrifuged four times with distilled water, then vacuum-filtered, dried, and X-rayed to confirm removal of all calcite.

Inductively coupled plasma-atomic emission spectroscopy was used to determine the Sr, Na, Fe, and Mn contents of the dolomite. Pure dolomite powders (100 mg) were reacted overnight in 6*M* HCl and then heated for 1 h at 90 °C to insure complete digestion. Detection limits for Sr, Mn, Fe, and Na were 5 ppm, 0.25 ppm, 4.7 ppm, and 36.2 ppm, respectively, with precisions of  $\pm 8$  ppm,  $\pm 6$  ppm,  $\pm 18$  ppm, and  $\pm 33$  ppm, respectively. All petrophysical and geochemical data are available in the GSA Data Repository.<sup>1</sup>

To assess the spatial pattern of each measured variable, the semivariance of each attribute as a function of distance between samples (lag) was calculated according to the method of Deutsch and Journel (1998). This analysis utilizes every analytical measurement. Patterns in semivariance  $(\gamma)$  as a function of lag reflect the nature and extent of spatial organization in the data. Herein, the important geostatistical parameters include (1) the amount of semivariance at the minimum lag (30 cm), which quantifies sample-to-sample scatter; (2) the distance (correlation range) over which the value of a variable is similar to adjacent points; and (3) the relative amount of semivariance at lags greater than the correlation range, which quantifies longer spatial patterns.

Because spatial patterns can be structured but not periodic, periodicities and white noise in the lateral patterns of each measured variable were determined by Lomb-Scargle spectral analysis (Press et al., 1992), which accounts for data that are not evenly sampled



Figure 2. Semivariograms depicting average variability ( $\gamma$ ) as function of separation distance (lag) between samples. Arrows denote near-random component at minimum separation distances. Gray lines mark correlation ranges (r, in meters).

(i.e., gaps in the 30 cm sample spacing). The spectral analysis was done on a five-point moving average of each variable, which filters the data to highlight the spatial patterns. As permeability scales logarithmically, the moving average utilized log permeability. The autoregressive red-noise model of Schulz and Mudelsse (2002) was used as the null hypothesis in assessing whether spectral peaks were significant.

# RESULTS

Figure 1 shows the lateral patterns in porosity, permeability, Sr, Na, Fe, and Mn for the Madison dolowackestone. Each attribute shows a large amount of sample-to-sample scatter, but the five-point moving averages through each data set show laterally oscillatory patterns.

The semivariance analyses (Fig. 2) reveal that each measured variable in the Madison dolomite has a near-random component at a lag of 30 cm that accounts for 50%–70% of the total observed variability. Permeability and Na exhibit the greatest amount of randomness (68% and 71%, respectively) and Mn the least (50%). The high sample-to-sample vari-



Figure 3. Periodiograms generated by spectral analysis of five-point moving averages in Figure 1. A: Porosity and log permeability. B: Na and Sr. C: Fe and Mn. Horizontal long dashed lines are white-noise models; short dashed lines are red-noise models. Peaks with spectral powers above red noise are statistically significant at the 95% confidence level, and their periods are labeled in meters. Peaks that would be significant at slightly lesser red-noise confidence levels are labeled in gray.

ability exhibited by all parameters produces the large amount of scatter in Figure 1. The variables exhibit correlation ranges (r) of 2.3– 7.3 m, indicating that there is short-scale structure within each data set. Lastly, each variable also exhibits long-range oscillatory patterns in semivariance at sample separation distances greater than those correlation ranges. These long-range patterns equate to 11%–23% of the total semivariance. Permeability and porosity exhibit the least long-range oscillations, whereas Sr, Na, and Mn exhibit the greatest (Fig. 2).

At the 95% confidence level, there is at least one significant periodicity in each data set, as evidenced by the spectral analyses (Fig. 3) of the five-point moving averages. Porosity, permeability, Sr, and Fe exhibit significant periodicities between 1.2 and 2.4 m. A suite of periodicities >3.2 m also occurs in the Fe, Mn, Sr, and Na data. At lesser red-noise significance levels, there would also be significant periods at 8.5 m in porosity and permeability, and 24.2 m in Mn. There are

<sup>&</sup>lt;sup>1</sup>GSA Data Repository item 2006074, petrophysical and geochemical data, is available online at www.geosociety.org/pubs/ft2006.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.

periodicities (Fig. 2) that are identical or very similar to correlation ranges (Fig. 1) for porosity, permeability, Sr, Na, and Fe, which reinforces that the spatial structure is indeed periodic.

Collectively, the figures demonstrate that there is a nested pattern of periodic, oscillatory spatial variation in the chemical and petrophysical properties of the Madison dolowackestones. These patterns are embedded within a large amount of random variance, but the oscillatory patterns are real and represent  $\sim$ 30%–50% of the variability observed in any one attribute. Given that similar patterns occur in permeability distributions within the San Andres dolomites, these laterally oscillatory patterns might be a previously unrecognized property of all dolomites.

# POTENTIAL ORIGINS OF LATERAL PERIODICITY

Three different hypotheses could individually or in combination explain the laterally periodic oscillations in the petrophysical and trace-element signatures of the Madison dolowackestone. They could be either (1) a pattern inherited from the dolomite's precursor; (2) a result of formation during late diagenesis by the addition of dolomite cement and/or recrystallization; or (3) patterns produced during initial dolomitization by self-organizing phenomena. Further work involving two- and three-dimensional characterizations of dolomite attributes, equivalent spatial analysis of modern sediments, experimental reaction modeling, and sampling across preserved dolomitization fronts not affected by later diagenesis will be needed to test these hypotheses.

# **Inherited Template**

If a number of depositional attributes were at least partially oscillatory, then inheritance of those oscillations might be the origin of the petrophysical and geochemical patterns observed in the dolomite. For example, lateral oscillations in the original abundance of Srrich aragonite bioclasts and oxyhydroxides might occur due to sorting by storm waves. Dissolution of those bioclasts and mobilization of the oxyhydroxides during dolomitization might have preserved the same oscillatory patterns in the abundance of molds (affecting porosity, permeability) and dolomite trace-element contents (Sr from the bioclasts, Fe and Mn from the oxyhydroxides).

We consider inheritance from the precursor to be the least likely of the plausible explanations. Countless diagenetic studies have shown that dolomitization resets the chemistry and fabric of the precursors. Support for that argument includes the massive import of Mg

and resetting of  $\delta^{18}$ O values, indicating that the chemistry of dolomitizing systems is water buffered. Lateral patterns in the abundance of trace elements due to inheritance (rock buffering) would thus be difficult to explain. If available, Fe and Mn are added to dolomite due to partitioning coefficients >1, whereas Sr and Na are exported due to partitioning coefficients <1. Similarly, the conversion of micron-sized lime mud or micrite to decimicron-sized dolomite means a complete restructuring of fabric and texture, and thus a reorganization of pore networks. Due to the wholesale restructuring of the rock that accompanies dolomitization, it seems unreasonable to argue that oscillatory patterns in petrophysical and geochemical properties could be inherited.

# **Postdolomitization Diagenesis**

Diagenesis after initial dolomitization is the second possible origin for oscillatory patterns in the attributes of dolomites. The Madison dolowackestones exhibit a dull red luminescence with multiple generations of crystal growth (i.e., subtly zoned luminescence). The cores of some, but not all, rhombs also exhibit patchy luminescence indicative of dolomite recrystallization. Crocket (1994), Sonnenfeld (1996), and Moore (2001) argued that all zones in the rhombs formed in association with Mississippian reflux dolomitization. If so, then dolomite-to-dolomite recrystallization is the only significant burial feature, and that process could only have affected the traceelement patterns, not the petrophysical patterns. In such a case, burial alteration alone would not account for all oscillatory patterns.

However, if the outermost crystal zones formed by cementation during burial, then the oscillatory patterns in both physical and chemical attributes could result from the combined lateral variations in the relative amounts of dolomite recrystallization and dolomite cementation. In such a case, the oscillations might be due to the spacing of fractures that acted as fluid conduits, or the availability of pore space within the dolomites for cements to grow within. A late diagenetic origin for the oscillatory patterns is a hypothesis that cannot be rejected or accepted without confirming that the outer zones of the dolomite rhombs are indeed burial products, and without detailed information on the lateral abundance of those cements and recrystallization products.

## Self-Organization During Dolomitization

Any geochemical system characterized by reaction-transport phenomena may develop repetitive patterns in the absence of a precursor pattern (Ortoleva, 1994). Self-organization develops one pattern from all possible patterns and amplifies it into well-ordered, observable structures. The results can be expressed in a variety of descriptive variables, including textural, chemical, mineralogical, and petrophysical attributes (Ortoleva et al., 1987a; Ortoleva, 1994). Examples in sedimentary rocks include oscillatory zoning within crystals, nucleation and crystal ripening, chemical banding of cements and mineral phases, and reaction-front fingering in diagenesis and karsting (Ortoleva et al., 1987a; Chen et al., 1990; Ortoleva, 1994).

Pulses in fluid flow or fluid chemistry during migration of the dolomitization front might cause feedback loops within the reaction-transport process, producing patterns where none existed before. Although the pulses may be externally driven (e.g., climate change), the pattern forms as the dolomitization front migrates through time and thus is an example of self-organization.

A very common self-organizing feature in diagenesis is reaction fingering, in which positive feedbacks occur between initial porosity and permeability heterogeneities and subsequent changes in rock properties due to dissolution-precipitation reactions (Ortoleva, 1994). This in turn can lead to precipitationinduced flow diversion and the refocusing of the flow past the precipitated mass. A spot pattern in dolomite attributes might evolve due to alternations between less porous "overdolomitized" rock and more porous "underdolomitized" rock. A single horizontal transect through the dolomite body would yield the oscillatory patterns seen in Figure 1, regardless of whether the flow was normal or parallel to the bed.

Self-organizing phenomena during dolomitization may be the most reasonable explanation for the observed oscillatory patterns in the attributes of the Madison dolomites. Reaction fingering is a well-documented process during fluid flow through sediments and rocks that have a heterogeneous distribution of porosity and permeability, which the dolomite's precursor most certainly had. Large-scale numerical simulations of dolomitization (Potdevin et al., 1992; Jones and Xiao, 2005) predict lateral patterns in porosity and permeability. As noted here, dolomitization dramatically changes the precursor's chemistry and fabric, thus it is logical to assume that any patterns in those attributes are the product of dolomitization. Due to differences in distribution coefficients, self-organization should lead to different periodicities in each trace element, as is observed. Further, overdolomitization and underdolomitization patterns would have different effects on porosity and permeability, as the sealing of a pore throat may minimally affect the former and dramatically affect the latter. Porosity and permeability would thus be predicted to have slightly different spatial characteristics, as is observed.

# POTENTIAL SIGNIFICANCE

There has been negligible analysis of the lateral properties of dolomites at the decameter scale, yet our data indicate that there are laterally periodic oscillatory patterns in both chemical and physical attributes. These features have up to now been unrecognized, and addressing their origin and meaning(s) represents a new approach to the study of dolomites. The recognition of oscillatory patterns in dolomites and understanding their origin also has other significant implications.

The attributes of dolomite samples from vertical sequences are routinely used as proxies for early Earth's carbon budget and climate (e.g., Kaufman et al., 1991; Kennedy, 1996) and/or various types of Phanerozoic geologic processes related to fluid flow, mass transfer, and basin history. However, if 30%–50% of an attribute's variability in a single bed is due to laterally oscillatory patterns, one must ask if that lateral variability is too great to assume a single sample is representative of a particular horizon.

The oscillatory patterns in porosity and permeability can affect pore connectivity and fluid flow, even when scatter composes most of the petrophysical variance (Jennings et al., 1998; Pranter et al., 2005). Thus, those oscillatory patterns should be understood, so that they can be incorporated into models of multiphase fluid flow in dolomite reservoirs and contaminant transport from matrix to conduits in dolomite aquifers.

If the oscillatory patterns are selforganizing phenomena, then they can be used to interpret ancient dolomitizing systems in ways previously not realized. The geometry and anisotropy of self-organized properties depend on the nature of the precursor flow units, flow directions, and diagenetic fluids (Ortoleva et al., 1987b; Chen and Ortoleva, 1990; Potdevin et al., 1992). If the nature of the precursor can be constrained by facies analysis, and the composition of the diagenetic fluid is constrained by the general geochemistry of the dolomite, then inverse reaction-transport modeling of the oscillatory patterns should define paleo-fluid-flow vectors at the scale of tens to hundreds of meters and the migration rate of the dolomitizing front.

# ACKNOWLEDGMENTS

This research was supported by the University of Colorado's (CU) Reservoir Characterization and Modeling Laboratory and CU's Council on Research and Creative Work. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for additional financial support. Burlington Northern and Santa Fe Railway Corporation and the U.S. Bureau of Land Management granted permission to access and obtain samples in Sheep Canyon.

# **REFERENCES CITED**

- Budd, D.A., 2001, Permeability variation with depth in the Cenozoic carbonate platform of westcentral Florida, USA: American Association of Petroleum Geologists (AAPG) Bulletin, v. 85, p. 1253–1272.
- Chen, W., and Ortoleva, P.J., 1990, Reaction front fingering in carbonate-cemented sandstones: Earth-Science Reviews, v. 29, p. 183–198, doi: 10.1016/0012-8252(90)90036-U.
- Chen, W., Ghaith, A., Park, A., and Ortoleva, P., 1990, Diagenesis through coupled processes: Modeling approach, self-organization, and implications for exploration, *in* Meshri, I., and Ortoleva, P., eds., Prediction of reservoir quality through chemical modeling: American Association of Petroleum Geologists Memoir 49, p. 103–130.
- Crocket, J.J., 1994, Porosity evolution of the Madison Limestone (Mississippian): Wind River Basin, Wyoming [M.S. thesis]: Baton Rouge, Louisiana, Louisiana State University, 103 p.
- Deutsch, C.V., and Journel, A.G., 1998, GSLIB, a geostatistical software library and user's guide (2nd edition): New York, Oxford University Press, 369 p.
- Eisenburg, R.A., Harris, P.M., Grant, C.W., Goggin, D.J., and Conner, F.J., 1994, Modeling reservoir heterogeneity within outer ramp carbonate facies using an outcrop analog, San Andres Formation of the Permian Basin: American Association of Petroleum Geologists (AAPG) Bulletin, v. 78, p. 1337–1359.
- Grant, C.W., Goggin, D.J., and Harris, P.M., 1994, Outcrop analog for cyclic-shelf reservoirs, San Andres Formation of the Permian Basin: Stratigraphic framework, permeability distribution, geostatistics, and fluid-flow modeling: American Association of Petroleum Geologists (AAPG) Bulletin, v. 78, p. 23–54.
- Jennings, J.W., Jr., 2000, Spatial statistics of permeability data from carbonate outcrops of West Texas and New Mexico: Implications for improved reservoir modeling: Bureau of Economic Geology, University of Texas, Report of Investigation 258, 50 p.
- Jennings, J.W., Ruppel, S.C., and Ward, W.B., 1998, Geostatistical analysis of petrophysical data and modeling of fluid-flow effects in carbonate outcrops, *in* Society of Petroleum Engineers Annual Technical Conference and Exhibition, New Orleans, September 27–30, 1998: Richardson, TX, Society of Petroleum Engineers: SPE Paper 49025, 16 p.
- Jones, G.D., and Xiao, Y., 2005, Dolomitization, anhydrite cementation, and porosity evolution in a reflux system: Insights from reactive transport models: American Association of Petroleum Geologists (AAPG) Bulletin, v. 89, p. 577–601, doi: 10.1306/12010404078.
- Kaufman, A.J., Hayes, J.M., Knoll, A.H., and Germs, G.B., 1991, Isotopic compositions of carbonates and organic carbon from Upper Proterozoic successions in Namibia: Stratigraphic variations and the effects of diagenesis and metamorphism: Precambrian Research, v. 49, p. 301–327, doi: 10.1016/0301-9268 (91)90039-D.

- Kennedy, M.J., 1996, Stratigraphy, sedimentology, and isotopic geochemistry of Australian Neoproterozoic post glacial cap dolostones: Deglaciation,  $\delta^{13}$ C excursions, and carbonate precipitation: Journal of Sedimentary Research, v. 66, p. 1050–1064.
- Kerans, C., Lucia, FJ., and Senger, R.K., 1994, Integrated characterization of carbonate ramp reservoirs using Permian San Andres Formation outcrop analogs: American Association of Petroleum Geologists (AAPG) Bulletin, v. 78, p. 181–216.
- Moore, C.H., 2001, Carbonate reservoirs: Porosity evolution and diagenesis in a sequence stratigraphic framework: Amsterdam, Elsevier, Developments in Sedimentology 55, 444 p.
- Ortoleva, P.J., 1994, Geochemical self-organization: Oxford Monographs on Geology and Geophysics 23, 411 p.
- Ortoleva, P.J., Merino, E., Moore, C., and Chadam, J., 1987a, Geochemical self-organization, I: Reaction-transport feedbacks and modeling approach: American Journal of Science, v. 287, p. 979–1007.
- Ortoleva, P.J., Chadam, J., Merino, E., and Sen, A., 1987b, Geochemical self-organization, II: The reactive-infiltration instability: American Journal of Science, v. 287, p. 1008–1040.
- Potdevin, J.L., Chen, W., Park, A., Chen, Y., and Ortoleva, P., 1992, CIRF: A general reactiontransport code: Mineralization fronts due to the infiltration of reactive fluids, *in* Kharaka, Y., and Maest, A., eds., Water-rock interaction: Rotterdam, Balkema, p. 1047–1050.
- Pranter, M.J., Hirstius, C.B., and Budd, D.A., 2005, Multiple scales of lateral petrophysical heterogeneity within dolomite lithofacies as determined from outcrop analogs: Implications for 3-D reservoir modeling: American Association of Petroleum Geologists (AAPG) Bulletin, v. 89, p. 645–662, doi: 10.1306/ 11300404049.
- Press, W.H., Teukolsky, S.A., Vetterling, W.T., and Flannery, B.H., 1992, Fourier and spectral applications, *in* Press, W.H., et al., eds., Numerical recipes in Fortran—The art of scientific computing (2nd edition): Cambridge, Cambridge University Press, p. 530–602.
- Schulz, M., and Mudelsse, M., 2002, REDFIT: Estimating red-noise spectra directly from unevenly spaced paleoclimatic time series: Computers & Geosciences, v. 28, p. 421–426, doi: 10.1016/S0098-3004(01)00044-9.
- Smith, L.B., Jr., Eberli, G.P., and Sonnenfeld, M.D., 2004, Sequence-stratigraphic and paleogeographic distribution of reservoir-quality dolomite, Madison Formation, Wyoming and Montana, *in* Grammer, G.M., Eberli, G.P., and Harris, P.M., eds., Integration of outcrop and modern analogs in reservoir modeling: American Association of Petroleum Geologists Memoir 80, p. 94–118.
- Sonnenfeld, M.D., 1996, Sequence evolution and hierarchy within the Lower Mississippian Madison Limestone of Wyoming, *in* Longman, M.W., and Sonnenfeld, M.D., eds., Paleozoic systems of the Rocky Mountain region: Denver, CO, Rocky Mountain Section SEPM (Society for Sedimentary Geology), p. 165–192.

Manuscript received 3 August 2005 Revised manuscript received 16 December 2005 Manuscript accepted 20 December 2005

Printed in USA