Seafloor-precipitated carbonate fans in the Neoproterozoic Rainstorm Member, Johnnie Formation, Death Valley Region, USA

Sara Brady Pruss *,a, Frank A. Corsetti b, Woodward W. Fischer c

Department of Geology, Smith College, Northampton, MA, 01063, United States
Department of Earth Sciences, University of Southern California, Los Angeles, CA 90089-0740, United States
Division of Geological and Planetary Sciences, Caltech, Pasadena, CA 91125, United States

A R T I C L E   I N F O

Article history:
Received 6 March 2007
Received in revised form 26 February 2008
Accepted 13 March 2008

Keywords:
Aragonite
Precipitates
Ediacaran
Carbon cycle

A B S T R A C T

Cm-sized carbonate sea floor fans occur in the Neoproterozoic Rainstorm Member of the Johnnie Formation, Death Valley, USA. The fans formed in a mixed carbonate-clastic succession near storm wave base at the base of parasequences on a storm-dominated ramp. Petrographic observations indicate that the fans were originally precipitated as aragonite and later inverted to calcite during diagenesis. Although not directly dated, the Rainstorm Member preserves a large magnitude negative carbon isotopic anomaly (down to ~11‰, PDB) tentatively correlated to the largest known carbon isotope excursion found in many stratigraphic successions around the world between 585 Ma and 550 Ma. Thus, the age distribution of sea floor aragonite fans in Neoproterozoic strata appears more widespread than previously thought, occurring in strata significantly younger than the last widespread Neoproterozoic glaciation. Rainstorm Member carbonate fans and oolitic units (representing time-correlative shallower environments) record similar carbon isotope ratios during the negative carbon isotopic anomaly. The carbon isotopic homogeneity displayed between fans and other carbonate sediments implies that waters across the shelf were well-mixed rather than stratified during the late Neoproterozoic isotopic anomaly. In addition, the similarity of carbon isotope ratios shared among fans along a stratigraphic horizon (on a m- to cm-scales) suggests that the local source of alkalinity required for fan growth was derived from a well-mixed reservoir, likely seawater, rather than local diageneric fluids. Increased alkalinity and the presence of inhibitors to carbonate nucleation (perhaps Fe²⁺ under anoxic conditions) likely fostered precipitation of aragonite crystal fans on the seafloor.

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1. Introduction

Calcium carbonate seafloor fans are unusual features of the geologic record, and the conditions that fostered their formation are still poorly understood. Carbonate fans are common features of Archean and Paleoproterozoic carbonate platforms (Kah and Knoll, 1996; Sumner and Grotzinger, 1996b; Sumner and Grotzinger, 2000), and are conspicuous features of carbonates that cap low latitude glacial deposits of the Neoproterozoic (e.g. Kennedy, 1996; Hoffman et al., 1998; Hoffman and Schrag, 2002). In the Phanerozoic, similar fans are known to form in reef cavities and other restricted diageneric environments (e.g. James et al., 1988), but carbonate fans precipitated directly on the seafloor appear to be quite rare. One notable exception occurs in Lower Triassic strata, deposited in the aftermath of the largest extinction in the history of life. The stratigraphic distribution of carbonate fans suggests that specific environmental factors play a role in their development and preservation and that these features in post-Proterozoic successions form as a result of transient, rather than sustained (~1 myr), environmental conditions.

Here we report sea floor-precipitated carbonate fans preserved in the Rainstorm Member of the Ediacaran Johnnie Formation, Death Valley region, eastern California. The fans occur in cm-sized beds that formed in a mixed carbonate-clastic succession. The Rainstorm Member was deposited on the shelf near storm wave base. The Rainstorm Member records a very large negative carbon isotopic anomaly, correlated by Kaufman et al. (2007) to similar anomalies documented in South Australia, Oman, Namibia and South China tentatively and dated between 585 Ma and 550 Ma (e.g. Calver et al., 2004; Condon et al., 2005; Fike et al., 2006; Le Guerroue et al., 2006). In contrast to associated ooids and micrite that can be transported after precipitation, carbonate fans are definitive recorders of sea floor oceanic conditions. The purpose of this project was to ascertain the environmental conditions that fostered aragonite fan development in the Rainstorm Member. Furthermore, a better understanding of the processes and environmental conditions surrounding the development of sea floor carbonate fans should ultimately provide insights into carbon
cycle dynamics of the Ediacaran world, particularly during incursion of the largest known marine carbon isotopic anomaly (e.g., Calver et al., 2004; Fike et al., 2006; Le Guerroue et al., 2006; Kaufman et al., 2007).

2. Geologic setting and stratigraphy

The Johnnie Formation is a component of the Neoproterozoic section (Fig. 1a) of the Death Valley region in the western United States (here informally termed the Death Valley succession). The Neoproterozoic Death Valley succession records the transition from continental rifting to passive-margin sedimentation (Stewart, 1970; Stewart, 1991). Diabase sills that intrude the underlying Crystal Spring Formation (found stratigraphically well below the Johnnie Formation) are 1.08 Ga (Heaman and Grotzinger, 1992), forming a robust lower age constraint. The Neoproterozoic–Cambrian boundary in the overlying Wood Canyon Formation (Corsetti and Hagadorn, 2000) inferred via correlation to be ca. 543 Ma (Bowring et al., 1993; Grotzinger et al., 1995) places an upper constraint. Other constraints exist, but they are less robust, given that our understanding of Neoproterozoic Earth stratigraphy is still in flux. For example, the Johnnie Formation is located well above glacially influenced strata in the Kingston Peak Formation that may correlate with other glacial deposits, between ~723 Ma and 580 Ma (e.g., Brasier et al., 2000; Bowring et al., 2003; Allen et al., 2004; Fanning and Link, 2004). Workers have used sequence stratigraphy to correlate incised
The Johnnie Formation has been subdivided into seven sequences with the Rainstorm Member comprising the upper part of sequence five (siltstones), the entirety of sequence six (from the Johnnie Oolite to a prominent incision, including the fans), and the lower portion of sequence seven (Summa, 1993) (Fig. 1c). The Rainstorm Member is approximately 150 m thick in the Nopah Range and contains, from base to top, green siltstone, a prominent oolite marker bed (the Johnnie Oolite), interbedded reddish siltstone and sandstone, pink precipitate-bearing limestones, and additional siliciclastic strata. The carbonate seafloor fans of the Rainstorm Member were previously reported but were not described in detail (Summa, 1993). This study focuses on the occurrence of the seafloor fans in Summa’s sequence six.

3. Sedimentology of the Rainstorm Member

The best-developed fans were studied at the Western Talc Mine (WTM) and Nopah Range localities (NR) in the Southern Nopah Range area (Fig. 1d). The majority of sequence six above the Johnnie Oolite is best exposed at the Nopah Range locality (Summa, 1993). At these sections, the Rainstorm Member was measured and described, and precipitate-bearing limestone units were sampled (Table 1). The base of the measured section in the Nopah Range begins ~7.8 m from the top of the Johnnie Oolite above hummocky cross-stratified sandstones and interbedded siltstones (Fig. 2a). In general, the succession consists of orange and red hummocky cross-stratified fine sandstone and siltstone with mud-draped ripple marks near the tops of some units. Prominent intraclastic precipitate-bearing limestones are intercalated throughout the section. The majority of the limestones are pink; the precipitate layers form cm-scale grey beds (Fig. 1c) and are concentrated in the lower half of the section. The grey precipitate beds commonly form on subtle erosional surfaces and pinch and swell along strike. Other distinctive sedimentologic features include edgewise conglomerates (Fig. 2c), concentrated in the upper half of the section.

Table 1

<table>
<thead>
<tr>
<th>Unit</th>
<th>Thickness</th>
<th>Lithologies and sedimentary structures</th>
<th>Carbon isotope values</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.6 m</td>
<td>Pink and orange laminated fine sandstones and siltstones</td>
<td>X2–1: 9.72, X2–2: 9.90, X11–1: 9.18, X11–2: 10.35, X11–3: 10.70, X11–4: 10.98, X4–2: 10.70, X4–3: 10.65, X4–4: 10.82</td>
</tr>
<tr>
<td>B</td>
<td>8.3 m</td>
<td>Pink and orange sandstones and siltstones with calcareous horizons that form resistant ledges and are interbedded with thinner (30–40 cm thick) non-resistant siltstone beds.</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2.1 m</td>
<td>Pink and grey limestones that contain five separate cm-scale precipitate beds near the top of the unit (X1–X5). The precipitate-bearing limestones are predominantly grey in color and the limestone beds with precipitates are pink (Fig. 2b).</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>2.1 m</td>
<td>Thin-bedded siltstones; Tops of beds are rippled and mud draped. Precipitate bed caps unit (X6)</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>0.2 m</td>
<td>Pink limestones that contain grey precipitate layer. The precipitate bed pinches and swells along strike; the contact at the base of the precipitate bed is erosional. (X7)</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>1.3 m</td>
<td>Red siltstones</td>
<td></td>
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<tr>
<td>G</td>
<td>2.5 m</td>
<td>Pink limestones with smaller grey beds; basal 1 cm is grey limestone with precipitates overlain by intraclasts; thin calcareous siltstone and mudstone beds are intercalated; the upper 0.8 m contains hummocky cross stratification. (X8–X9)</td>
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<tr>
<td>H</td>
<td>1.1 m</td>
<td>Siltstones intercalated mud-drapped ripple marks. In the upper 20 cm, there is an alternation between layers of orange calcareous rip-ups in a silty matrix and limestone with possible precipitate fabrics (X10)</td>
<td></td>
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<tr>
<td>I</td>
<td>3.6 m</td>
<td>Orange siltstones with minor thin calcareous horizons and mud-drapped ripple marks.</td>
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<tr>
<td>J</td>
<td>0.8 m</td>
<td>Limestones with edgewise conglomerates at base; hummocky cross-stratified siltstone crops out in middle of unit and siltstone with calcareous intraclasts caps unit.</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>3.3 m</td>
<td>Non-resistant siltstone capped by precipitate unit</td>
<td></td>
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<tr>
<td>L</td>
<td>2.3 m</td>
<td>Pink limestones that contain a cm-scale grey precipitate layer at base; unit is cross-stratified with intraclasts near top, possible precipitate bed at top. (X11–X12)</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>2.2 m</td>
<td>Orange and dark red siltstones and sandstones that grades into mudstones at top; Edgewise conglomerate exposed 0.8 m above the base; The edgewise conglomerates are composed of upwardly oriented stacks of flat clasts (long axis ~3 to 5 cm).</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.2 m</td>
<td>Pink limestones with grey cm-scale precipitate bed at base (last precipitate-bearing bed in this section). (X13)</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>6.7 m</td>
<td>Siltstones with small limestone bed that contains an edgewise conglomerate.</td>
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</table>
3.1. Stratigraphic interpretations

The Johnnie Oolite is interpreted to have formed in shallow-water agitated conditions (Summa, 1993). Massive and planar laminated siltstones overlying the oolite are thought to represent deepening during initial flooding on a sequence boundary, and the hummocky cross-stratified sandstones and limestones that overlie the oolite suggest storm-dominated shelf deposition (Summa, 1993). Most thin precipitate beds are overlain by siltstones; this coupling likely represents a small-scale deepening followed by shallowing. Deposition of the fans most likely occurred during times of low environmental energy (Winefield, 2000). The precipitated beds consists of small, delicate crystals precipitated on the seafloor, therefore, it is likely that they formed in relatively quiet conditions. The fans have not been found broken or abraded, suggesting quiet water conditions persisted until burial. The fact that the limestones associated with the
precipitate beds contain some hummocky cross-stratification and intraformational and edgewise conglomerates suggests that the precipitate beds were formed during quiescent periods between storm events, and/or that the initial deepening represented by the precipitate beds occurred below storm wave base. The edgewise intraclast conglomerates indicate early, and perhaps rapid, lithification of the seafloor (Mount and Kidder, 1993). The erosional surfaces on which many of these fans formed record flooding surfaces at the base of higher order parasequences.

4. Petrographic and analytical methods

Samples of the seafloor precipitate-bearing limestones were collected and thin-sectioned. These thin-sections were examined to determine the original mineralogy of the precipitates, their microscopic forms, and the minerals associated with the carbonate precipitates. Thin-sections were examined under transmitted light, reflected light, and via SEM equipped with an energy-dispersive spectroscopy (EDS) system. To constrain the source of alkalinity for the seafloor-precipitated fans in the Rainstorm Member, carbonate carbon isotope ratios (\(\delta^{13}C_{\text{carb}}\)) were measured along several stratigraphic horizons containing crystal fans. Samples were microdrilled where preservation of the fans enabled sampling of individual precipitates within a single bed (Table 1). Carbon isotope ratios were measured on a VG Optima gas source mass spectrometer and are reported relative to a PDB standard.

5. Seafloor fans of the Rainstorm Member

The precipitate-bearing units occur within centimeter-sized limestone beds that are overlain by siliciclastic units. The precipitates apparently grew both as radiating crystals (fans) and as “beds” of upward-oriented crystals (e.g., Sumner and Grotzinger, 2000) that are typically one centimeter in height. The crystal units (originally bundles of aragonite crystals) occur both in clusters (Fig. 2f) and evenly spaced across a bedding plane (Fig. 2e). Growth forms of the crystals vary from dense patches to sparsely spaced units across bedding planes. This may be evidence for the precipitates growing as fans (Fig. 2d) in some beds, but as individual crystals on the seafloor in others (Fig. 2e).

In vertical cross-section, the crystal size is variable. At their base, most crystals average ~ 100 µm in diameter and expand to ~200 µm at their termination. The crystals range in length from about 0.1 to 3.0 cm. The crystals display square terminations (Fig. 2f). Small, subangular to subrounded opaque grains (~10–50 µm in diameter) and ooids (200–300 µm) are found in the interspaces between the crystals, and precipitate beds are commonly overlain by beds of intraclasts. Each crystal is composed of a mosaic of smaller equant calcite subunits (Fig. 2f and g) with diameters on the order of 10–30 µm. In horizontal thin-section, the crystals have a hexagonal cross-section with a maximum diameter of 230 µm (Fig. 2g). As in the vertical cross-section, the interstices between the crystals are filled with ooids, intraclasts, and small opaque grains. Reflected light microscopy and EDS analysis indicate that the opaque grains are iron-rich. These grains do not cut across individual carbonate crystals and are primarily concentrated in fan-bearing horizons. Commonly, the fans nucleated on concentrations of opaque grains atop minor erosional surfaces, micritic intraclasts, and/or hardgrounds (Fig. 2h). Iron-rich crusts are also found along the edges of micritic clasts, indicating coeval precipitation. Units that underlie or overlie the fan beds have few iron minerals and do not contain fans.

Carbon isotopes were measured from 15 individual precipitate units from 4 horizons (Table 1). Values were compared to units within the same bed as well as between beds. Carbon isotopes of the precipitates are similar to values reported from interbedded carbonates (Corsetti and Kaufman, 2002).

5.1. Original mineralogy of the fan beds

The fans are currently composed of calcite, but their form suggests that the original composition was aragonite. The crystal units have hexagonal cross-sections, acicular growth forms, and blocky to square terminations (Fig. 2f–h) which are consistent with aragonite precipitation (Louch and Folk, 1976; Mazzullo, 1980; Sandberg, 1985; James and Choquette, 1990; Sumner and Grotzinger, 2000). The crystal units also consist of an interlocking mosaic of equant calcite, commonly produced during aragonite inversion to calcite (Sandberg, 1985; Wilkinson et al., 1985). Finally, in comparing these fans with seafloor-nucleated gypsum, it is clear that spear-like terminations typically exhibited by gypsum crystals are not seen in these beds (Klein and Hurlbut, 1993).

From field and thin-section analyses, pink and grey limestones and pinkish siltstones and sandstones are common features of the Rainstorm Member. This color may be derived from the presence of oxidized iron and/or manganese. Grains clustering around individual crystals in thin-section were reddish-black in color, and an SEM-EDS analysis of these minerals showed distinctly high iron peaks (Pruss and Corsetti, 2002). The minerals are now iron oxides, and it is difficult to determine their original mineralogy; however, based on the shape of the grains, these minerals may have originally formed as pyrite and were subsequently oxidized, although the EDS analyses did not record the presence of sulfur in appreciable amounts. The iron-rich grains were deposited (or precipitated) between the fans as they grew, because they do not cross-cut any of the fans in thin-section.

6. Discussion

6.1. Geologic distribution of carbonate fans

Carbonate fans are common features in early Precambrian successions but become increasingly environmentally restricted through the Meso- and Neoproterozoic sedimentary record. Seafloor-precipitated carbonates formed commonly in Archean and Paleoproterozoic marine basins, implying that the nature of carbonate sedimentation and ocean carbonate chemistry must have been fundamentally different from modern conditions. In Mesoproterozoic carbonate successions, fans are restricted to intertidal environments (Bartley et al., 2000). For the remainder of the Precambrian era, seafloor-precipitated carbonates are generally rare; however, they do appear in enigmatic carbonates often superposed with glacial deposits (e.g. Kennedy, 1996; Hoffman et al., 1998; James et al., 2001; Hoffman and Schrag, 2002). In particular, aragonite fan pseudomorphs deposited in cap carbonates of the Mackenzie Mountains also formed in limestone beds within siliciclastic-dominated settings (James et al., 2001). In the Phanerozoic rock record, the most conspicuous seafloor fans occur in Lower Triassic sections following a major mass extinction (Woods et al., 1999; Pruss et al., 2006). Similarly sized carbonate fans in the modern are now restricted to diagenetic environments (e.g. James et al., 1988) and are not known to occur in open marine conditions on the seafloor. The stratigraphic distribution of carbonate fans, their overall rarity in post-Proterozoic successions, and their occurrence in otherwise enigmatic carbonates (i.e. Snowball Earth and Lower Triassic carbonates) suggests that rare environmental factors are required to foster their formation. A better understanding of specific fan occurrences in the geologic record might ultimately provide insight into why fans form where they form.

6.2. Conditions fostering fan formation

Carbonate fans of the Rainstorm Member formed in a storm-dominated shallow subtidal setting. Fans occur in limestone beds interbedded with siliciclastics. Carbonate sediments of the Rainstorm Member include ooids, micrite, and edgewise intraclasts in addition to
carbonate fans. The crystal fans likely formed rapidly and were buried prior to destruction by storm or other currents. The abundance of iron minerals in the interstices of the fans suggests formation of iron minerals occurred from ambient seawater or during early diagenesis; this suggests that reduced iron was available and abundant in bottom waters, perhaps as anoxic waters bathed the seafloor, during fan formation. The presence of iron associated with seafloor fans is interesting given suggestions that iron and other inhibitors of carbonate nucleation played an important role in driving the precipitation of seafloor crystal fans (Sumner and Grotzinger, 1996a; de Leeuw, 2002).

In addition to the local paleoenvironmental conditions that fostered fan formation, regional and/or global oceanic conditions may have also played a role. The fans were precipitated on the seafloor at the sediment–water interface, likely in an anoxic environment. Two sources for the alkalinity are possible for the precipitation of carbonate fans: the water column and the sediments. Diagenetic reactions (driven by the remineralization of sedimentary organic matter) occurring within fan-associated sediments may have created alkalinity that diffused to the sediment–water interface, providing carbonate ions for fan growth. Such reactions would include anaerobic respiration of organic matter using iron and manganese oxides, nitrate, or sulfate as electron acceptors. In part because diffusion is slow, the spatial scale of organic matter remineralization within sediments leads to cm-scale heterogeneity in carbon isotopic composition of DIC within the pore fluid (Irwin et al., 1977; Hennessy and Knauth, 1985; Mazzullo, 2000). If such a process supplied the alkalinity required for seafloor fans, individual fans would record a similar isotopic heterogeneity. In contrast, if the alkalinity was sourced from the water column, the DIC pool should be well-mixed isotopically (because the rates of organic remineralization processes are slower relative to advective mixing in the surface ocean).

Given that the carbon isotopic values for the Rainstorm fan samples are similar within a single bed (+/−0.6%) as well as between beds (+/−9.14 to −11.18%), and that their values correspond with those measured from associated oolitic carbonates (Corsetti and Kaufman, 2003), a diagenetic sedimentary source of alkalinity seems unlikely. Rather, the source of alkalinity was probably a well-mixed, isotopically-depleted oceanic seawater source that bathed the seafloor above storm wave base, at or near the mixing zone. Furthermore, as the fans formed during initial transgression at the base of parasequences, they may record the isotopic composition of relatively deeper water conditions. The agreement between the isotopic composition of seafloor-precipitated fans and overlying shallow carbonates, suggests that the biological pump was not providing a distinct deep alkalinity source for the precipitation of the fans (e.g. Hotinski et al., 2001). The isotopic correspondence between the relatively deeper water fans and overlying carbonates suggests that the isotopic composition of the seawater within this sedimentary basin was homogeneous during the large carbon isotopic anomaly.

The presence of iron minerals concentrated in the interstices of fan units may provide an important clue about fan formation. EDS analysis of these minerals suggest that these are rich in iron and are now currently iron oxides. It is possible that when these minerals formed, they formed as pyrite (a product of reduced iron) and were later oxidized. Regardless of their original mineralogy, the abundance of iron in carbonate fan beds suggest that, like the source of alkalinity, iron was delivered as dissolved Fe$^{2+}$ in the water column, perhaps acting as a transient inhibitor to micrite under anoxic conditions (de Leeuw, 2002). This analysis of Rainstorm fans suggest that the presence of anoxic waters during transgression fostered a seafloor mode of precipitation and that the alkalinity required for fan development was supplied from a well-mixed water column. Future work is required to determine if the environmental conditions that fostered iron-rich carbonate fans are unique to the Rainstorm Member or if these features are common to seafloor carbonate fans from other sedimentary basins of this age, and, ultimately, additional intervals in Earth history.

7. Conclusions

The seafloor carbonate fans in the Neoproterozoic Rainstorm Member of the Johnnie Formation formed in a shallow subtidal storm-dominated setting. Evidence of abundant iron-bearing minerals associated with the fan suggests that dissolved iron may have acted as a periodic inhibitor of carbonate nucleation, favoring precipitation directly on existing nuclei on the seafloor. Carbon isotope ratios of the seafloor crystal fans indicate that these facies record the same strongly $^{13}$C-depleted isotopic composition as correllative shallow water carbonate facies. These data lend support for the hypothesis that alkalinity required for seafloor aragonite fan growth advected from a well-mixed water column source, rather than diffused from anaerobic diagenetic reactions occurring in the sediments (Fike et al., 2006; Le Guerroue et al., 2006). Robust age constraints are generally lacking from much of the Neoproterozoic–Cambrian stratigraphy exposed in Death Valley; however, the stratigraphic position of the Johnnie Formation occur well above glacial deposits (Prave, 1999; Corsetti and Kaufman, 2003; Corsetti et al., 2007) and during a large, possibly global, carbon isotopic excursion of probable Ediacaran age (e.g. Calver et al., 2004; Fike et al., 2006; Le Guerroue et al., 2006; Kaufman et al., 2007). In light of this, the Rainstorm Member currently contains the youngest known occurrence of calcium carbonate fans in the Proterozoic. A better mechanistic understanding of such unusual carbonate facies will ultimately provide insights into the formation of carbonate fans during this and other anomalous intervals in Earth history.

Acknowledgments

The authors would like to thank C. Summa for her helpful comments regarding this research and Dan Schrag’s laboratory at Harvard University for stable isotope analysis. S. Pruss would like to thank K. Hanks, D. DeSewert, and M. Fraiser for help in the field. Helpful comments and discussion by P. Marenco, M. Clapham, N. Lorentz, J. Bartley, I. Montañez, M. Vogel, A. Knoll, and N. James on a previous version of this manuscript were greatly appreciated.

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