Dolomite abundance in the North American rock record

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Abstract

The mineral dolomite (CaMg(CO3)2) forms in only small quantities in modern oceans, cannot be precipitated abiotically from unmodified seawater in laboratory experiments, yet comprises much of the carbonate rock record. The challenge of explaining the apparent temporal discrepancy in dolomite, the "dolomite problem," has fascinated carbonate sedimentologists for centuries. Yet, this pursuit has lacked a quantitative tabulation of dolomite in the rock record. Here, we use the North American rock record, as archived in Macrostrat, to assemble a record of dolomite abundance through geologic time. The completeness and age resolution of our dataset allow us to compare dolomite abundance with environmental variables, including stromatolite abundance, evaporite occurrences, sea level, glaciation, and temperature. We use these comparisons to test the assumption that the bulk of the geologic dolomite record was formed via secondary diagenetic processes. We find no monotonic decrease in abundance with age-the expected result if late diagenesis affects the bulk of the record. Dolomite was just as abundant during the first half of the Paleozoic as it was during most of the Neoproterozoic, a challenge to canonical thinking. We show that a number of dolomite precipitation mechanisms known from modern environments and experimentally grown dolomite can explain many of the patterns we observe in the North American dolomite record. Perhaps dolomite is not such a problem after all.

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The mineral dolomite ($CaMg(CO_3)_2$) forms in only small quantities in modern oceans, cannot be precipitated abiotically from unmodified seawater in laboratory experiments, yet comprises much of the carbonate rock record. The challenge of explaining the apparent temporal discrepancy in dolomite, the "dolomite problem," has fascinated carbonate sedimentologists for centuries. Yet, this pursuit has lacked a quantitative tabulation of dolomite in the rock record. Here, we use the North American rock record, as archived in Macrostrat, to assemble a record of dolomite abundance through geologic time. The completeness and age resolution of our dataset allow us to compare dolomite abundance with environmental variables, including stromatolite abundance, evaporite occurrences, sea level, glaciation, and temperature. We use these comparisons to test the assumption that the bulk of the geologic dolomite record was formed via secondary diagenetic processes. We find no monotonic decrease in abundance with age – the expected result if late diagenesis affects the bulk of the record. Dolomite was just as abundant during the first half of the Paleozoic as it was during most of the Neoproterozoic, a challenge to canonical thinking. We show that a number of dolomite precipitation mechanisms known from modern environments and experimentally grown dolomite can explain many of the patterns we observe in the North American dolomite record. Perhaps dolomite is not such a problem after all.

dolomite | Macrostrat | stromatolites
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Introduction

Carbonate rocks regulate Earth's carbon cycle and temperature by storing CO_2 on long timescales, and preserve our best archive of the physical, chemical, and biological characteristics of surface environmentsthroughout Earth history. However, the chemical composition of these sediments ($(Ca,Mg,Fe)CO_3$) makes them sensitive to chemical overprinting and alteration by diagenetic (secondary) fluids, including hydrothermal and meteroric water. Dolomitization, the conversion of calcite or aragonite (both $CaCO_3$) to dolomite ($CaMg(CO_3)_2$), is a particularly widespread yet incompletely understood diagenetic process. Anecdotal evidence derived from observations (e.g., 1) and tabulated estimates suggest that over 50% of carbonates in many geologic time periods are dolomite (2, 3, and references therein). To leverage the fact that the carbonate rock record preserves a rich archive of shallow marine environments across Earth history, to use dolomites as effective paleoenvironmental proxies, it is imperative we know where, why, and how they formed. Is dolomite primarily a diagenetic mineral that preserves information about sub-surface secondary processes, or can the geochemical signals preserved in geologic dolomite reflect conditions on Earth's surface?

Historically, there have been two primary challenges to understanding the genesis of dolomite in the geologic record: very little dolomite forms in marine settings today, and it has proven very difficult to abiotically precipitate stoichiometric, ordered dolomite in laboratory settings from unmodified seawater (4). To explain the volumes of geologic dolomite while accounting for these challenges, it is commonly thought that much of the dolomite in the geologic record is diagenetic in origin, forming via the conversion of primary $CaCO_3$ to $MgCa(CO_3)_2$ long after deposition (e.g., 5, 6). There is certainly ample evidence for this type of dolomite in the rock record (e.g., 5, 7, and many others); late diagenetic dolomite is often fabric-destructive, obliterating primary depositional crystal fabrics and textures (7, 8), and dolomitization fronts that crosscut facies and early diagenetic features across limestone ($CaCO_3$) outcrops provide solid evidence that this style of dolomite formation was responsible for some, if not most, of the massive dolomite observed in the rock record (9).

However, the (few) examples of modern dolomite (e.g., 10–12), a suite of recent lab studies (e.g., 13, 14), and fine-grained, fabric-preserving geologic dolomite (e.g., 1, 3, 8, 15, 16) all hint that other, non-diagenetic, processes may have contributed to the formation of some of the dolomite in the rock record, too. Microbial ecosystems are increasingly thought to play a crucial role in the formation of modern – and perhaps ancient – dolomite, possibly in conjunction with environmental variables like heat and high salinity (10–12, 17). Petrographic observations of Neoproterozoic (1000-541 Ma) carbonates have also been used to suggest that primary dolomite precipitated abiotically in Precambrian oceans in much the same way that aragonite does in the modern (16). Aridity and evaporation may also promote dolomite precipitation in both ancient (18, 19) and modern settings (20, 21). It is not uncommon to find papers, especially from the 1960s, that interpret supra- to intertidal dolomites – the final facies in a shoaling cycle – as primary precipitants or penecontemporaneous diagenetic products, and dolomites are often reported to co-occur with evaporitic minerals (e.g., 18, 22, 23).

Although we know that dolomite can form via these numerous pathways, we still lack a solid understanding of which of these dolomite-forming mechanisms produced volumetrically significant amounts of dolomite throughout geologic time. To approach this problem, previous workers have compiled tabulations of the relative abundance of dolomite through time (2, 24–27). While early studies found that older rocks tended to be more dolomitic than younger rocks and cited this observation as evidence that all volumetrically significant dolomite is diagenetic, more recent studies have found correlations between dolomite abundance and environmental variables like sea level (2) and ocean anoxic events associated with mass extinctions (27), suggesting that the record of dolomite abundance through time can serve as a proxy for primary Earth system changes. However, each of these prior dolomite abundance studies either lacks completeness (e.g. the compilation by Given and Wilkinson contains one Cambrian sample), does not extend into the Precambrian (2, and references therein), only samples a limited amount of geologic time (1, 3), or cannot ensure unbiased sampling of the geologic record (1–3, 27).

Here, we compile a new record of dolomite abundance through time using Macrostrat (28) and use it to ask: how can a record of dolomite abundance through time inform our understanding of the physical, chemical, and biological processes occurring in shallow marine environments throughout Earth history? By combining this record with other known changes to the Earth system throughout Earth history, we can start to tease apart what dolomite-forming processes were important when. In turn, we can use these results to understand how the environments preserved in dolomitic rocks changed through time. Our approach ensures a high degree of completeness and aims to eliminate bias (i.e., we consider every named stratigraphic unit on the North American continent and do not hand select units nor rely on search engines to identify dolomitic sections).

Methods

We assembled our record of dolomite abundance through geologic time using all North American rock units in Macrostrat, accessed using the API. Units in this database are sourced primarily from the Correlation of stratigraphic units of North America (COSUNA) charts (17,045 units; 29) and Geology and economic minerals of Canada (4,316 units; 28). These sources likely represent a nearly-complete picture of the surface and subsurface geologic record across the continent, although the granularity and precision and accuracy of age constraints of these compilations may mean there are some missing or inaccurately dated units in Macrostrat. However, these errors are likely small compared to the number of units in Macrostrat (n=27,034) – a benefit of using large datasets. Indeed, Macrostrat has been shown to agree with the broad trends observed in Ronov et al. (30)'s map-based estimate of global sedimentary rock volume (31), and concerns that the geologic record may be a net record of erosion have been assuaged by patterns and trends in rock volume in the Macrostrat database (28, 32). Thus, the rock record as represented in Macrostrat reflects patterns of deposition that can be used to study Earth history on long timescales (28, 31–33).

To estimate dolomite abundance relative to the prevalence of all carbonate rocks through time, we rely on the temporal, spatial, and compositional data associated with most units in Macrostrat. A continuous time age model – applied to all units – ensures temporal agreement across laterally and vertically adjacent geologic entities to 1 Myr precision. All time bins used in our analyses are 1 Myr long. An example of the Macrostrat data for the Devonian-aged Sevy Formation is shown in Figure 1 alongside the total number of formations across the North American sedimentary record from 2000 million years ago (Ma) to present. By Macrostrat definition, a *formation*, a named stratigraphic entity (including named Members, Formations, and Groups), is comprised of at least one *unit*, the expression of a formation over one time-invariant area of Earth's surface (polygons in Figure 1a). As we will show, the distinction between units and formations is small for the dolomite record we have compiled (Figure 2).

We define *dolomite abundance* as the fraction of carbonate of a given age that is dolomitic. While this abundance fraction is unitless, we can calculate it using a variety of metrics in Macrostrat, including: thickness, area, and volume; and the binary presence or absence of dolomite in a unit, formation, or time interval (Figure 2). As we show in Figure 2, these metrics all generally collapse to the same trend. With considerations for future applicability of our work in mind, we use a formation-based dolomite abundance in most of our analyses, defined as:

$$f_{dol}^{fm} = \frac{\text{number of dolomite-bearing formations}}{\text{number of carbonate-bearing formations}}, \quad \textbf{(1)}$$

for every 1 Myr interval across the entire North American sedimentary record. The set of all dolomite-bearing

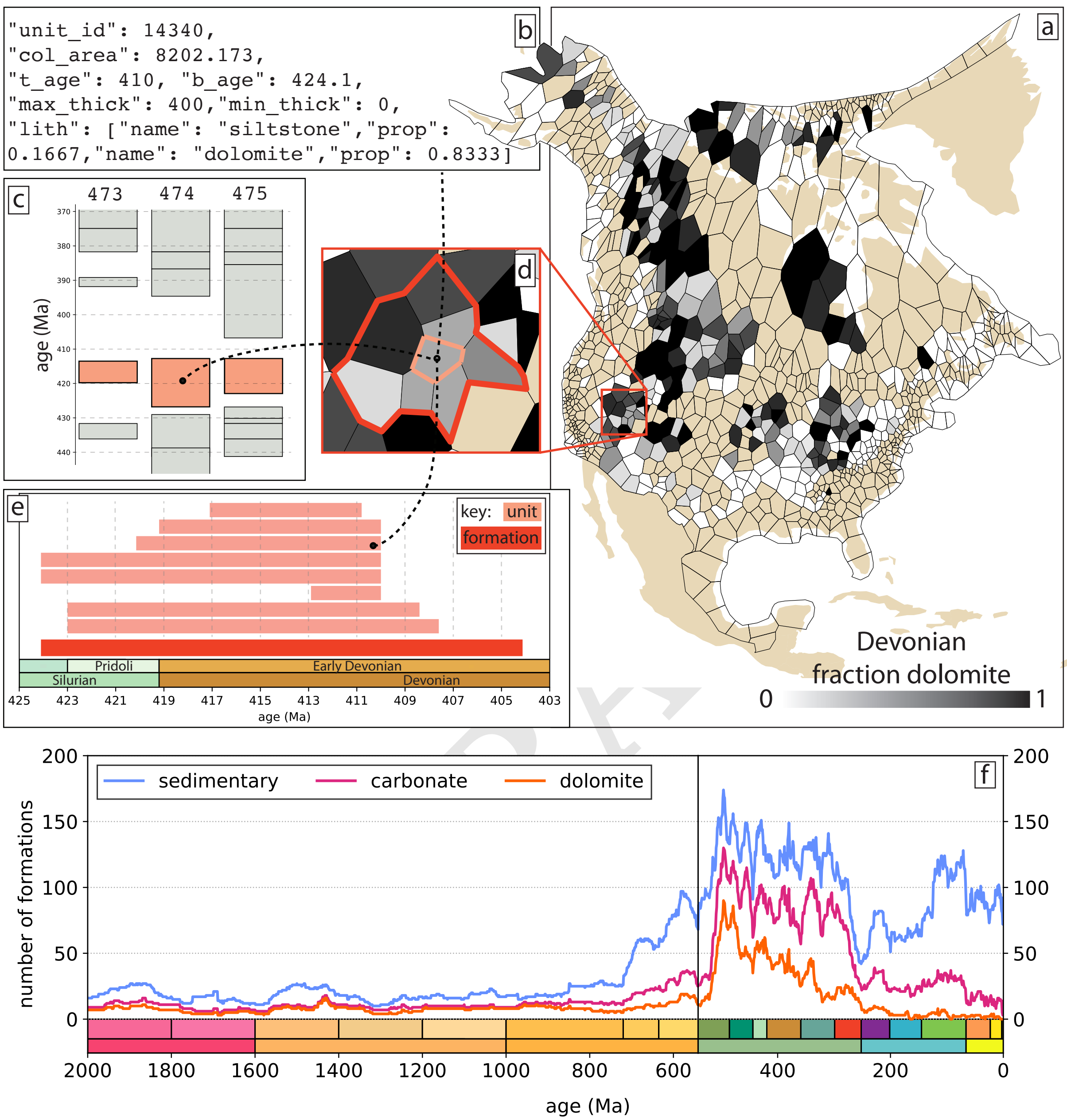

Fig. 1. Macrostrat data. a: Polygons, overlain on a tan-colored basemap of North America, divide the North American geologic record into time-invariant areas. All filled-in polygons contain Devonian-age carbonate and are shaded to represent the fraction of Devonian carbonate that is dolomitic. **b:** Selected data for one unit of the Sevy Formation, accessible via the Macrostrata API. `t_age` and `b_age` are top and bottom ages of the unit in Myr. `lith` = 'lithology'. **c:** Three columns that contain the Sevy Formation are highlighted in pink. Columns are time-invariant vertical slices through the crust; the surface expression of each column is one polygon in **a**. **d:** Detail of the Sevy Formation (highlighted in red), comprised of eight units (one unit per column/polygon). **e:** The eight units of the Sevy Formation plotted in time, displayed as pink bars. Each unit's top and bottom ages are constrained by the formation's age (represented by the longest, red bar) and the ages of other rock units in the column (e.g. grey boxes in **c**). **f:** Number of formations of sedimentary, carbonate, and dolomitic lithologies in Macrostrat, binned at 1 Myr resolution. All dolomites are carbonate and all carbonates are sedimentary.

formations is, by definition, contained in the set of all carbonate formations. We calculate f_{dol} by (1) identifying all carbonate-bearing formations that intersect a given 1 Myr time slice, and (2) identifying how many of those formations contain dolomite. We then expand from the binary nature of f_{dol} to ask how dolomitic any given dolomite-bearing formation is through time, a value we retrieve from the `lith` field of each Macrostrat unit or formation entry (Figure 1).

Estimating error. We also use the `lith` field to estimate the error in f_{dol}^{fm}. While every geologic entity in our compilation has some lithologic data attached to it, some entities have more than others. A total of 33 formations have a lithology only as specific as "carbonate" or "mixed carbonate-siliciclastic" – we do not have enough information to know if those carbonates are dolomitic or not. These poorly constrained formations represent only 1.05% of the 3145 carbonate formations in our dataset.

Other errors contained within f_{dol} could arise from some imprecision or inaccuracies in Macrostrat, including a formation's age (due to outdated or poor age constraints or errors in the Macrostrat age model), and a formation's lithology. In Figure 7, we use the multiple metrics in Macrostrat as an estimate of uncertainty around the multi-metric average $\bar{f}_{dol}$, another way to account for error in our record. A benefit of using the binary presence/absence of dolomite in a formation as our preferred metric: it does not matter how accurate Macrostrat's accounting of f_{dol} is in one formation – we care only that there *is* or *is not* dolomite.

Results

Dolomite abundance is highest during the Proterozoic, in some intervals reaching nearly 100% of carbonate, and lowest during the late Mesozoic and Cenozoic (Figure 2). However, f_{dol} does not monotonically decrease with age. Instead, we observe interesting, perhaps oscillatory, behavior from the mid-Neoproterozoic through early Paleozoic. After a Carboniferous low of $f_{dol} < 0.2$, a prominent Permian peak of ~ 0.4 serves as the last extended period of time during which dolomite comprised more than 20% of carbonate rocks. After the Triassic, both the absolute number of dolomite formations and the relative abundance of dolomite decrease dramatically: some intervals have zero dolomitic formations.

The North American rock record is characterized by late Paleozoic carbonates (> 100 carbonate-bearing formations per 1 Myr time bin); siliciclastic sediments comprise the majority of sedimentary rocks in both the late Neoproterozoic (717-540 Ma, > 50 siliciclastic formations per 1 Myr) and Meso- through Cenozoic (251-0 Ma, > 50 siliciclastic formations per 1 Myr) (Figure 1f). Although the latest Neoproterozoic and second half of the Phanerozoic have similar numbers of other carbonate and sedimentary formations (Figure 1f), they are distinctly different in the composition of carbonates – f_{dol} in the Cryogenian and Ediacaran periods is ~ 0.5, whereas it is < 0.2 for the Meso- and Cenozoic. Conversely, f_{dol} is statistically indistinguishable between consecutive periods from the Cryogenian through Silurian (Figure 3), despite the large increase in both the number of carbonate formations and the fraction of sedimentary formations that contain carbonate in the mid-Cambrian (Figures 1f, 2).

Discussion

We now seek to understand why we observe these features of the record: why dolomite is so abundant in Proterozoic strata, why f_{dol} oscillates around a consistent average of 0.5 from the Tonian through Devonian, why Carboniferous f_{dol} is so much lower than in the Devonian or Permian, and why dolomite is so uncommon after the Paleozoic. To do this, we compare our record of dolomite abundance to environmental variables (Figure 7), zoom in on some of the formations that comprise this record, and compare f_{dol} to stromatolite abundance as a proxy for either or both shallow marine environments and microbial mediation. We do not ascribe a dolomite-forming mechanism to all of the formations in our record; our "big data" approach to the dolomite problem reduces the need to do so, as we can make conclusions about aggregated data rather than at the scale of an individual formation. By comparing our record to environmental changes, by identifying changes in f_{dol} concurrent with other changes in deep time, we assess whether the dolomite record is dominated by late diagenetic dolomite – which we would not expect to correlate with environmental variables (34), or primary, penecontemporaneous, or early diagenetic dolomite, which would.

Proterozoic abundance. The ubiquity of dolomite in Precambrian successions is a commonly discussed phenomenon (8, 15, 16), and one our record corroborates. Existing hypotheses for why this is the case fall into two camps: Proterozoic f_{dol} is high because these carbonates are very old and have experienced many hundreds of millions of years of diagenesis (and the dolomite is mostly late diagenetic in origin) – an often mentioned, yet typically uncited claim (e.g., 15, 16) founded on studies of Phanerozoic dolomites (e.g., 24, 25, 34, 35), or because Proterozoic oceans – for some reason – promoted dolomite formation (and the dolomite is mostly early or primary: 1, 36). Petrographers have often noted that, at the microscopic scale, Precambrian

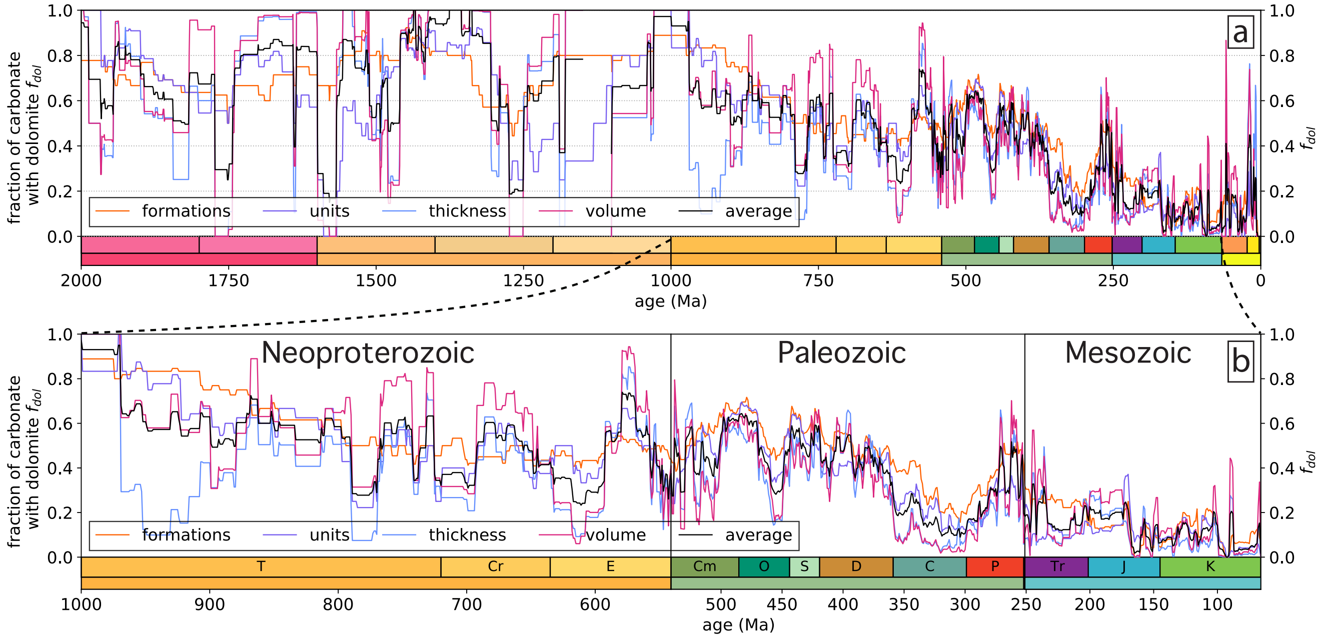

Fig. 2. Dolomite fraction through geologic time. f_{dol} calculated using four metrics: number of formations (orange), number of units (purple), thickness (blue), and volume (pink). The average of these four metrics is plotted in black. **a:** The complete record 2000 Ma - present. **b:** Neoproterozoic through Mesozoic era (1000-66 Ma).

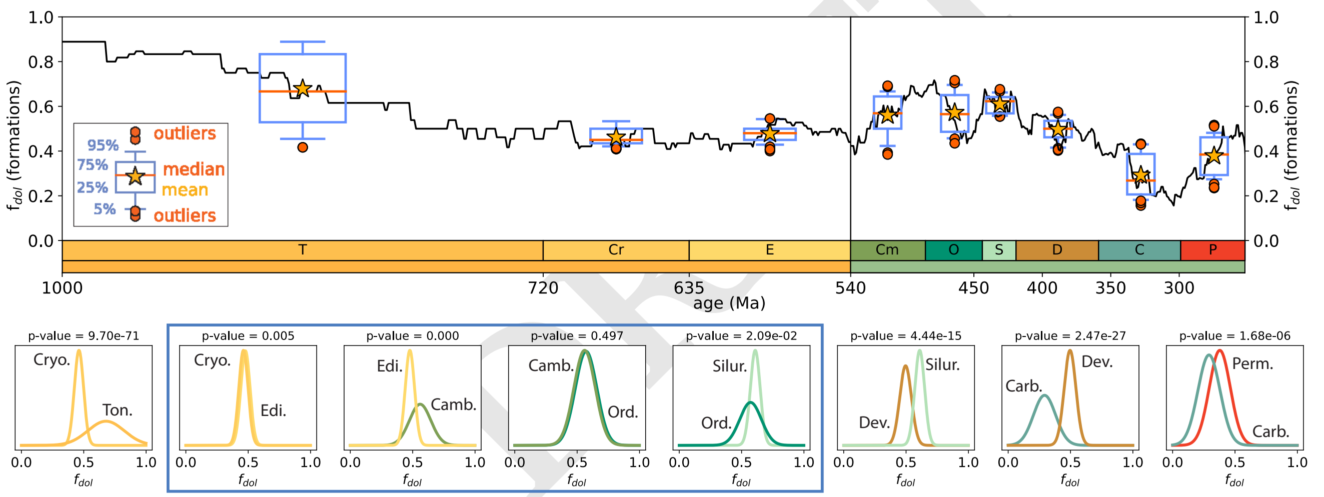

Fig. 3. Fraction of dolomite-bearing formations compared in consecutive periods. top panel: Box and whisker plots show period-level (e.g., Ediacaran, Cambrian) distributions of f_{dol}. **bottom panel**: Gaussian representations of the period-level distributions (calculated using the mean and standard deviation) are compared using the Kolmogorov-Smirnov test. We accept the null hypothesis that f_{dol} is drawn from the same distribution for the Cryogenian through Silurian periods.

dolomites tend to preserve primary fabrics and have fine crystals, an argument that these ancient dolomite are either early diagenetic replacements or primary precipitants – an argument for the latter hypothesis above (1, 3, 8, 15, 16, 37, 38). Challengingly, it is unclear what about Precambrian oceans would have promoted primary to early dolomite (higher or lower Mg/Ca (2), lower $[SO_4^{2-}]$ (39), and high dissolved silica (13) are all possibilities) and, before our compilation of f_{dol}, it had not been shown that Precambrian f_{dol} was quantitatively distinct from Phanerozoic dolomite abundance (although see 3).

We now observe that the assumption of high Precambrian f_{dol} is broadly true, but much more nuanced that previously discussed. Dolomite abundance is highest (and distinctly higher than during any interval in the Phanerozoic) from 2 Ga until the mid-Tonian ($\sim$ 900 Ma). From the late Tonian through the Devonian, f_{dol} is $\sim$constant at the period scale, with potential shorter-timescale fluctuations: to understand this 1 Gyr interval of elevated f_{dol}, we first construct a hypothesis to test whether late diagenetic dolomitization was responsible for converting primary Proterozoic $CaCO_3$ to $CaMg(CO_3)_2$. If it is the case that Proterozoic f_{dol} is high because the rocks are old and have seen

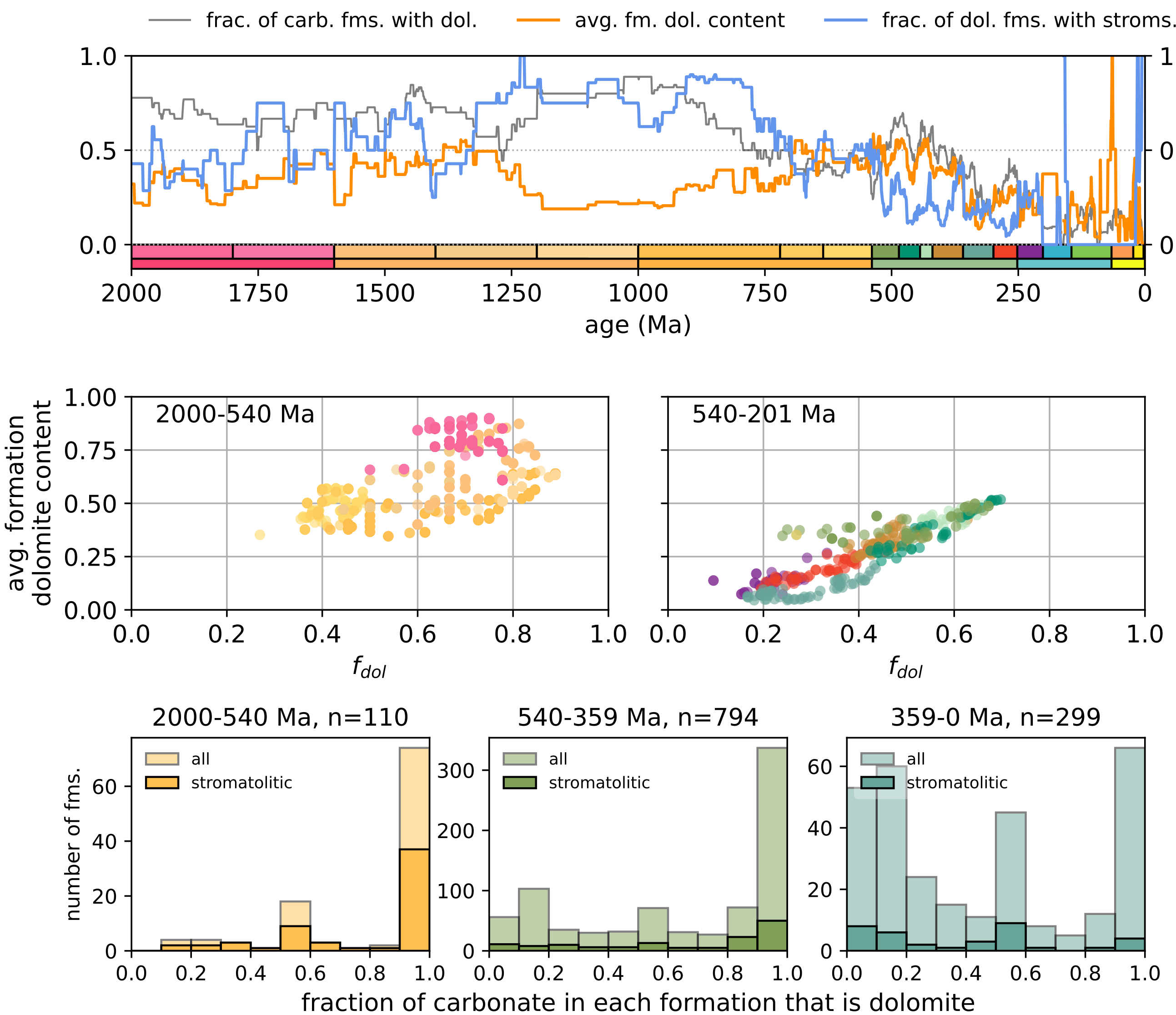

Fig. 4. How dolomitic are dolomite-bearing formations? Top: $f_{dol}^{fm.}$ plotted in grey, along with the fraction of dolomite-bearing formations that contain stromatolites (blue, f_{strom} in Figure 5), and the average dolomite content of dolomite-bearing formations in each 1Myr interval. **Middle:** Assessing the amount of dolomite in dolomite-bearing formations. Dots and colors as in Figure 5. Left panel: Proterozoic, right panel: Paleozoic-Mesozoic. In Phanerozoic time intervals with higher f_{dol}, formations also have higher dolomite content. **Bottom:** histograms showing how dolomitic dolomite-bearing formations are in three time intervals. Dark shaded portions are dolomite-bearing formations that contain stromatolites. The Proterozoic is dominated by formations that are 90-100% dolomite, and 50% of these dominantly dolomitic formations contain stromatolites. In the Phanerozoic, stromatolites are much less common in dominantly dolomitic formations.

hundreds of millions of years of dolomitizing diagenetic events, we would expect at least two things to be true: the carbonate in individual dolomite-bearing formations should be dominantly dolomitic, and dolomite abundance would not correlate with environmental variables (i.e., there is not a reason to expect late burial diagenetic dolomite to preferentially affect carbonates originally deposited only in certain environments).

Owing to the small number of Paleo- and Mesoproterozoic formations in the geologic record and their lack of macro-scale fossils for biostratigraphic correlation, we have an incomplete understanding of what Earth was like for this ~ 1 Gyr period of time. So, it is difficult to compare our record of dolomite abundance directly to paleoenvironmental changes, as we can in the Phanerozoic (Figure 7). We can, however, use other features of carbonate rocks to test the hypothesis that Proterozoic f_{dol} is (not) high because of environmental conditions unique to the Proterozoic. Here, we use the record of stromatolite abundance through time as a proxy for both paleoenvironment (stromatolites form in shallow marine environments) and dolomite formation mechanism (i.e., microbial mediation, see: 10, 14, 17, 40). We can't identify whether the co-occurrence of dolomite and stromatolites in carbonates is mechanistic (i.e., microbes that build stromatolites also precipitate or mediate the precipitation of dolomite), or environmentally coincidental (stromatolites grow and dolomite forms in the same depositional environments for different reasons). In either case, the dolomite formed would be, at the latest, early diagenetic: many studies of both modern and ancient shallow water carbonates have interpreted that dolomite found in these types of shallow water, stromatolitic sediments is primary, penecontemporaneous, or early diagenetic (11, 19, 23).

Comparing our f_{dol} record to the stromatolite abundance curve produced by Peters et al. 2017, we find that all Proterozoic formations have more closely associated stromatolites and dolomite that all Phanerozoic formations (Figure 5). We express this idea quantitatively in Figure 5 by plotting the fraction of dolomite-bearing formations that also have stromatolites (vertical axis, f_{strom}) against the fraction of carbonate formations that contain dolomite (horizontal axis, f_{dol}). In all Proterozoic periods 2 Ga - 540 Ma, $f_{strom} > 0.4$, while in all Phanerozoic periods 540-201 Ma, $f_{strom} < 0.3$. Additionally, most Proterozoic dolomite-bearing carbonate formations are 90-100% dolomite, and 50% of these almost entirely-dolomite formations are stromatolitic (Figure 4).

The co-occurrence of stromatolites and dolomite and the large fraction of very dolomitic formations that also contain stromatolites are intriguing observations – did microbial mediation produce much of the observed Precambrian dolomite? Below we interpret these records in the context of Phanerozoic carbonates as well.

Stromatolites. Although f_{strom} is lower in Phanerozoic than in Precambrian dolomites, it may still reflect the same phenomenon or process in both Eons: microbially mediated dolomite precipitation or early dolomite formation in shallow marine environments. To check that the co-association of stromatolites and dolomites that we show in Figure 5 is meaningful, we ground-truthed 10% of the identified overlapping formations (Figure 6). For dolomite and stromatolites to be truly co-occurring, the stromatolites must be described as lithologically dolomite (or the dolomite must be described as stromatolitic). We selected $\sim 10\%$ (25 of 223) of stromatolite-bearing formations at random and consulted the literature that describes each formation, searching for the lithology of microbial mats or stromatolites (Figure 6). Often, each formation only had a few papers that describe the lithology. In 3/25 cases, we could not find evidence of stromatolites; this error rate is as expected for the machine-reading algorithm written by Peters et al. (41) that identified stromatolite-bearing formations. In 12/25 cases, we found that the stromatolites are exclusively found in dolomite (and explicitly not found in co-occurring limestone). In two instances, stromatolites in one formation are both dolomitic and calcitic. In four cases, stromatolites are only calcitic. In the final four cases, too little descriptive information was found to

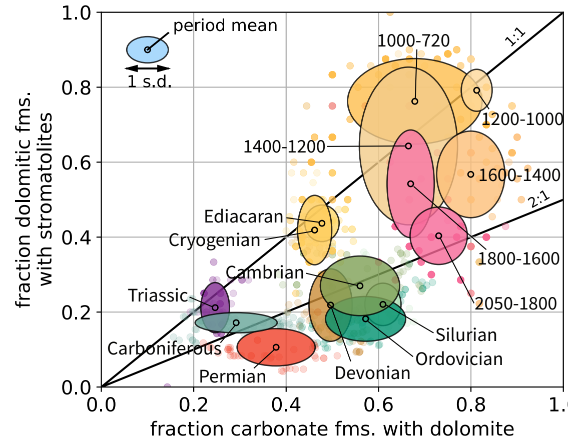

Fig. 5. Co-occurring stromatolites and dolomite. The fraction of carbonate formations that contain dolomite (f_{dol}, x-axis) and fraction of dolomitic formations that contain stromatolites (f_{strom}, y-axis). Stromatolite data from (41). Each dot represents the fractions in one 1Myr time bin and is colored based on the geologic time scale seen in other figures (e.g., Figure 2. Ellipses show period means with 1 std. dev.

determine the lithology of the stromatolities. We learn from this exercise that at least $14/25 = 56\%$ and up to $17/25 = 68\%$ of formations identified algorithmically contain dolomitic stromatolites. If stromatolites and dolomite co-occur at the formation level, it is more likely than not that the stromatolites are dolomitic.

So what does it mean that stromatolite-dolomite co-occurrence decreases from the Neoproterozoic to the Paleozoic? If this change reflects a decrease in the shallowest marine environments, we would not expect it to occur at the same time as peak carbonate abundance, which it does (Figure 1f). Instead, we suggest that the expansion of biomineralization during the Cambrian (e.g., 42) resulted in the apparent decrease in co-occurring stromatolites and dolomite by expanding carbonate shelf area[1] and total $CaCO_3$ volume, but via a new avenue of production less reliant on carbonate saturation state and ocean chemistry than Proterozoic carbonates. Stromatolites did not keep up with this expansion of carbonate area. Though they did increase in abundance briefly in the Cambrian (Figure 6), they represent a smaller fraction of marine carbonates than they did in the Proterozoic (41).

There are at least three conclusions we can draw from the observation that f_{strom} decreases at the Cambrian: (1) that this change means microbial mediation became less important for dolomite formation, (2) that shallow marine environments without stromatolites increased in abundance and dolomite was still formed in these depositional systems – the lack of co-occurring stromatolites has everything to do with stromatolite prevalence and nothing to do with dolomite, or (3) the carbonate precipitated by biomineralizers was more

[1]See our preprint of Bergmann, et al. 2022, *submitted* (DOI:10.1002/essoar.10511913.1).

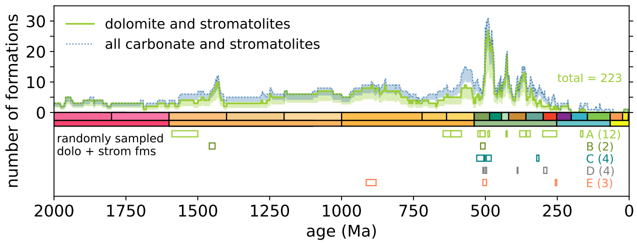

Fig. 6. Number of stromatolitic formations through time. **Top:** data from Peters et al. (41) for all carbonate formations (dashed blue) and only dolomitic formations (solid green). **Bottom:** results of ground-truthing exercise. A: stromatolites are dolomitic (n=12), B: stromatolites are both calcitic and dolomitic (n=2), C: stromatolites are only calcitic, D: could not find lithology, E: cannot confirm stromatolites. Horizontal extent of boxes reflect top and bottom ages of ground-truthed formations (vertical scale is meaningless).

susceptible to post-depositional dolomitization than the non-skeletal carbonates of the Proterozoic, resulting in proportionally more dolomite formed via diagenetic alteration (and proportionally less formed via microbial mediation). Evaluating these three hypotheses thoroughly will require a more granular dataset than the stromatolite (41) or dolomite records (Figure 2).

The Paleozoic. As Figure 3 illustrates, f_{dol} is statistically indistinguishable between consecutive periods across the Proterozoic-Phanerozoic transition, despite major changes to carbonate environments associated with the proliferation of $CaCO_3$ biomineralizing organisms. And, if a smaller number of dolomitic formations are also stromatolitic in the Paleozoic than Proterozoic, we must invoke a mechanism for forming this dolomite that relies less strongly on microbial communities.

As we did in the Proterozoic, we can investigate the possibility that much of the Paleozoic dolomite was formed via formation-scale dolomitiziation long after deposition. If this is the case, we would expect to find many nearly completely dolomitized formations, perhaps a larger proportion than in the Proterozoic. We do find a key difference in *how* dolomitic a dolomite-bearing formation is between the Proterozoic and Paleozoic: in the Paleozoic, when more carbonate formations contain dolomite (i.e., when f_{dol} is higher), each formation is more dolomitic (Figure 4c). In time intervals when f_{dol} is low (e.g., the Carboniferous), each dolomite-bearing formation contains very little dolomite. The same general observation can be made of Proterozoic data (Figure 4b), but the trend is much weaker.

Our earlier analysis suggested that microbial communities or stromatolitic environments may be important for forming some of the dominantly dolomitic formations in the Proterozoic (Figure 4d), but this relationship is less pronounced in the early Paleozoic (Figure 4e) and all but disappears in the rest of the Phanerozoic (Figure 4f). While 42% of early Paleozoic dolomite-bearing formations are 90-100% dolomite (337/794, Figure 4e), only 14.8% (50/337) of these dominantly dolomite formations contain stromatolites (versus 50%, 37/74, in the Proterozoic). These data suggest that the microbial co-occurrence with completely dolomitized formations is weaker in the Paleozoic, so we need an alternative mechanism to explain this dolomite.

Perhaps late burial dolomitization formed much of the Paleozoic (and especially early Paleozoic) dolomite. If this is true, late dolomitization would have been more prevalent in the Paleozoic than in the Proterozoic, so we require a property other than rock age to explain this phenomenon. Are skeletal Paleozoic carbonates more susceptible to dolomitization than non-skeletal Precambrian carbonates? Were diagenetic dolomitizing environments more prevalent on the North American craton than in the Proterozoic? Or, are there other, primary to early mechanisms that could explain the sustained high f_{dol} (and high average formation-level dolomite content) during the early Paleozoic?

Impacts of global environmental variables on dolomite abundance.

Evaporites. Many Recent dolomite forming environments are arid (11, 12, 20), and it is hypothesized that dolomite forms during the most evaporitic parts of the year (10, 11). Additionally, many ancient dolomites are anecdotally reported to be closely associated to evaporites (18, 19, 22), suggesting a causal link between evaporative, arid settings and dolomite formation (but see 43). Dolomite is thought to form in these settings via one of three mechanisms: primary physicochemical precipitation (e.g., 18, 20), primary microbially-mediated precipitation (e.g., 10, 11), or via seepage diagenesis (e.g., 44), which is thought to be the most common of the three (19).
To evaluate the impact of evaporative dolomite on the rock record, we tabulated the presence of evaporites in the `lith` field in Macrostrat (Figure 7). Evaporites are most common in the Paleozoic lithologic descriptions in Macrostrat and nearly absent in the Neoproterozoic – this may reflect a real signal, or could be due to less detailed lithologic descriptions for Neoproterozoic strata. Perhaps the most convincing link between f_{dol} and the presence of evaporites occurs during the Permian dolomite resurgence, when dolomites and evaporites are both concentrated in the southwestern United States (Figure 8; e.g., in the Rustler Formation, Salado Formation, and Alibates Formation)[2]

Sea level. In their 1987 record of dolomite abundance, Given and Wilkinson found a strong correlation between

[2]Explore Permian dolomite (`lith_id`= 31) and gypsum (`lith_id`= 36) formations in Macrostrat: via the API.

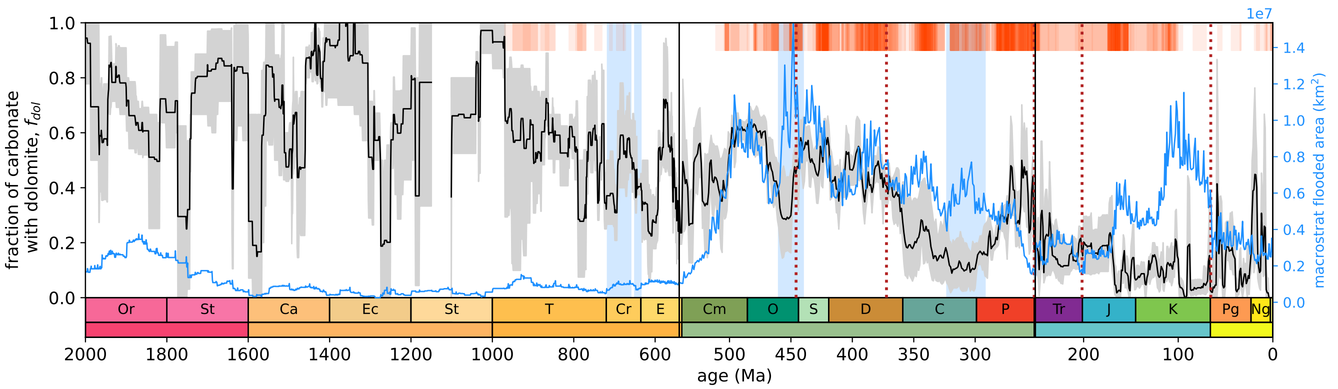

Fig. 7. Paleoenvironmetal indicators and dolomite abundance. Average f_{dol} (black line) shown with uncertainty (grey shading) determined by the lower and upper estimates from all Macrostrat metrics (shown in Figure 2). The area (in Macrostrat) covered by marine sedimentary rocks (blue line, right axis) is shown as an estimate of sea level across North America. Translucent red bars each represent 1 evaporite-bearing formation. Darker red = more evaporite-bearing formations. Blue vertical stripes highlight glacial intervals. Vertical dashed lines are placed at major mass extinctions.

dolomite abundance and global sea level. Here, we use the area covered by marine sedimentary rocks – the inundated area of North America in each 1 Myr time bin – as proxy for sea level across the continent, and find no correlation between dolomite abundance and sea level (Figure 7). Thus, we cannot confidently invoke a sea-level driven mechanism to explain the bulk of the dolomite record, though fluctuations in sea level may have been important on shorter timescales (e.g., in the late Cambrian-early Ordovician).

The 56 Myr Sloss sequences (45) in Paleozoic strata on North America are also missing in our dolomite record (Figure 2). These cycles, which Meyers and Peters (46) identified in the total marine sediment area in Macrostrat, are discernible in the timeseries of the number of carbonate formations shown in Figure 1f. While f_{dol} does vary on similar timescales during the Paleozoic, peaks in f_{dol} are not always correlated with peaks in the number of carbonate formations – in other words, just creating more carbonate rock does not guarantee more dolomite will form.

Anoxia. In their 2021 compilation of dolomite prevalence, Li et al. write that they find more dolomite during mass extinctions and ocean anoxic events. Our dolomite record – which utilizes a more statistically robust approach whereby we know the denominator of our dataset (all North American carbonates) – shows no correlation between mass extinctions and f_{dol} (dashed vertical lines in Figure 7). At the Cretaceous-Paleogene boundary, $f_{dol} \sim 0$; at the Triassic-Jurassic extinction, f_{dol} rises to its Mesozoic high of ~ 0.3; during the Frasnian-Famennian, f_{dol} is at a stable plateau of ~ 0.5; and at the end-Ordovician, f_{dol} is rising. The lack of a trend in our dataset means we have no reason to invoke the same mechanisms that gave rise to these mass extinction events (and associated ocean anoxic events) for the formation of dolomite at these intervals.

However, long-term atmospheric oxygenation patterns do have an intriguing imprint on the record of f_{dol}: broadly speaking, during the Paleo- and Mesoproterozoic, when f_{dol} reaches 1.0, atmospheric oxygen levels were lowest. A step increase in atmospheric oxygen is hypothesized to have occurred during the Neoproterozoic (when f_{dol} decreases to ~ 0.5), and again at the end Devonian (when, again, dolomite abundance decreases 47, 48). Anoxic conditions in the modern and in the laboratory have been demonstrated to promote dolomite formation, often in conjunction with microbial communities (10, 17). Perhaps the broadly stepwise-decreasing trend we observe in the Macrostrat record of f_{dol} in part reflects the stepwise-increasing oxygenation of Earth's atmosphere and thus the decline of anoxic environments in shallow marine settings.

Icehouse climates. In our final investigation of the record, we highlight two conspicuous lows in f_{dol}: the end-Ordovician ($\sim 460-445$ Ma) and Carboniferous-early Permian ($\sim 360-295$ Ma). During the prominent local minimum during the end-Ordovician, f_{dol} decreases from ~ 0.6 to ~ 0.2. The decline appears to start a few million years before the Hirnantian glaciation (blue bar in Figure 7) and recovery begins during the glacial. The Carboniferous period is the next prominent local minimum. There, f_{dol} falls from ~ 0.4 to ~ 0.1, again preceding a major glaciation, the Late Paleozoic Ice Age (LPIA, though there is evidence for short-term, regional glaciation before the peak ice age 49). Unlike the Quaternary icehouse climate, during the Hirnantian glaciation and LPIA, total carbonate abundance was high (Figure 1f) – dolomite seems to be uniquely impacted before and during these glacial epochs. So, the question arises: is the decrease in f_{dol} connected to the mechanisms responsible for initiating these glaciations?

Conclusions

Our Macrostrat-derived record shows that dolomite abundance does not decrease monotonically with age, challenging the assumption that most of the dolomite in the sedimentary record was formed by late burial diagenesis (34). Instead, we have demonstrated that there are intervals of time when f_{dol} varies with – and could be controlled by – environmental variables including the presence of stromatolites, evaporites, atmospheric oxygen levels, and glaciation. Notably, dolomite abundance is not correlated with sea level or mass extinctions, as other authors have found (2, 27). The co-occurrence of stromatolites in dolomitic formations (Figure 5) and the fact that this relationship changes with time suggests that microbial communities could have been especially important for the formation of Proterozoic dolomite, though this co-occurrence could be coincidental (and related to shallow water depositional environments) or mechanistic (via microbially mediated dolomite precipitation: 10, 12, 14, 17, 40). The correlations between f_{dol} and atmospheric oxygenation, and between f_{dol} and Paleozoic glaciations present intriguing possibilities for future mechanistic or kinetic investigations. The agreement and co-occurrence with environmental variables requires that we reconsider the assumption that most geologic dolomite was formed by secondary diagenetic processes. Instead, we suggest that many of the processes that produce dolomite in the Recent and in the laboratory could have been responsible for forming dolomite in deep time.

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Supplement

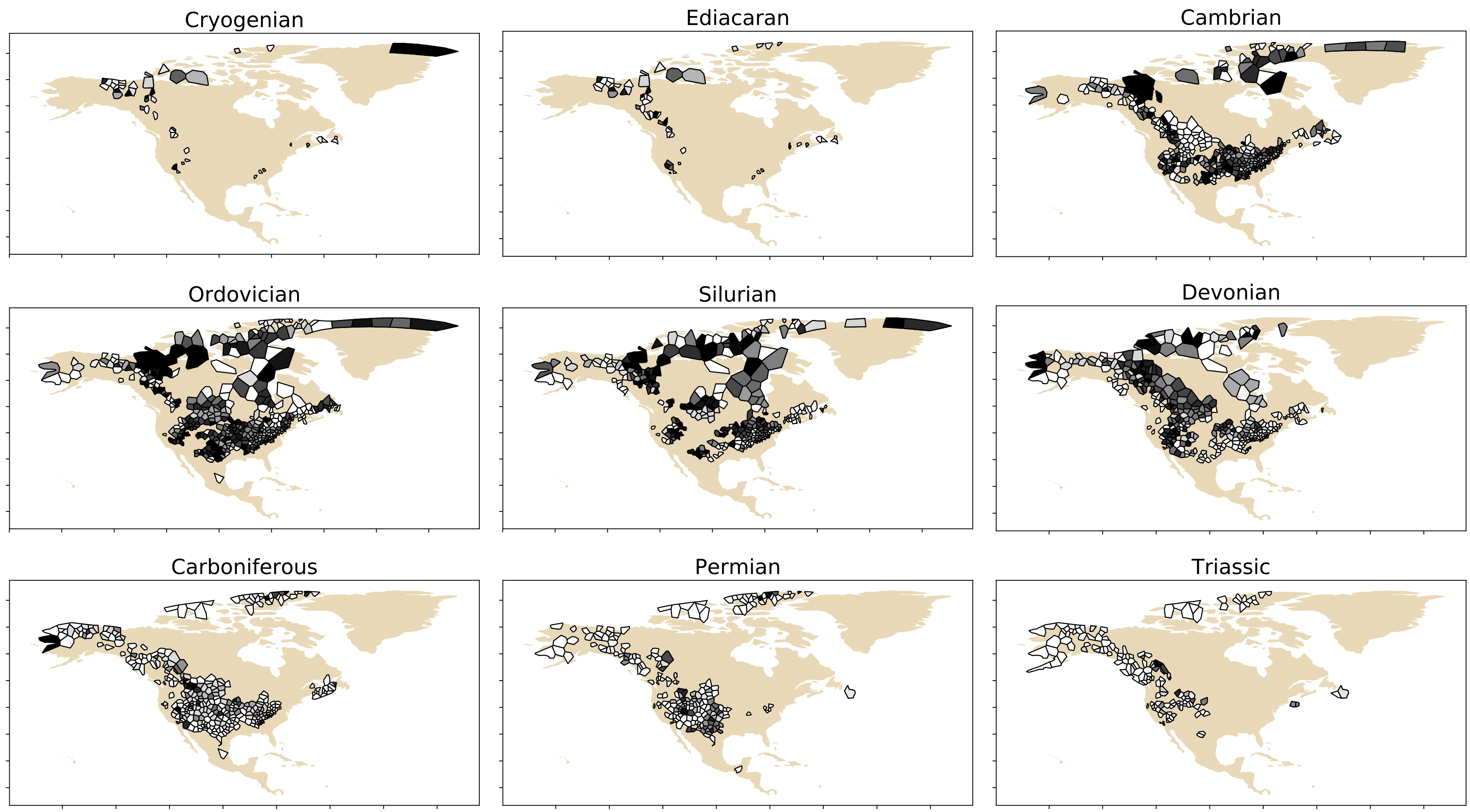

Fig. 8. Spatial distribution of dolomite through time. Averaged f_{dol} for each polygon over each period shown is plotted in black (100% of [period]-aged carbonate formations contain dolomite) to white (0% of [period]-aged carbonate formations contain dolomite). Only polygons that contain carbonate sediment are plotted. Tan basemap of modern-day North America is shown for reference.