



Dichotomous effects of oxidative metabolisms: A theoretical perspective on the dolomite problem

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ABSTRACT

The dolomite problem, which refers to the high abundance of dolomite in ancient geologic records in contrast to its scarcity in modern sediments, has been a century-long enigma in Earth science. Here I propose an explanation: the formation of carboxyl-rich oxidative metabolites (CROMs), which play a crucial role in dolomite precipitation, was favored by Earth's ancient oxygen-limiting environments but is inhibited under the modern oxygen-rich conditions. I first suggest the CROM hypothesis via a conceptual model, which predicts the dichotomous effects of oxidative metabolisms on dolomite production. I then reconstruct the evolutionary history of one representative CROM-producing enzyme family to test the hypothesis and show the temporal correlation between the variation in dolomite abundance on Earth's surface and the diversification of this enzyme family over geologic time. These results together suggest that the dolomite problem is a consequence of the intertwined environmental changes and biological evolution.

1. Introduction

Dolomite [CaMg(CO₃)₂] is a carbonate mineral that existed widely in ancient, especially Precambrian, sedimentary rocks but is seldom found in modern environments (Van Tuyl, 1916; McKenzie and Vasconcelos, 2009). This phenomenon, also called the “dolomite problem”, is an intriguing but long-standing enigma in Earth science (Van Tuyl, 1916; McKenzie and Vasconcelos, 2009). Different geological and biological factors, such as seawater chemistry (i.e., Mg/Ca ratio, dissolved CO₂, and SO₄²⁻ concentration, etc.) (Baker and Kastner, 1981; Burns et al., 2000; Tucker, 1982; Hood et al., 2011), temperature (Baker and Kastner, 1981; Sibley et al., 1987), and microbial activities (Petrash et al., 2017; Sánchez-Román et al., 2008; Li et al., 2018; Daye et al., 2019; Warthmann et al., 2000), have been suggested to influence the precipitation of dolomite, opening several windows through which to investigate the dolomite problem. However, geological and biological variables are interwoven; some experimental and field investigations have reported opposite observations, resulting in distinct interpretations (Brady et al., 1996; Sánchez-Román et al., 2009; Moreira et al., 2004). For example, some studies proposed that dolomite precipitation could be inhibited by sulfate ions (Baker and Kastner, 1981) and cation desolvation (Brady et al., 1996), while other research suggested that these factors are

unlikely to hinder dolomite formation (Sánchez-Román et al., 2009; Moreira et al., 2004). Nevertheless, the importance of one factor has become clear after intensive investigations in the past decades: dolomite formation at Earth's surface temperatures (lower than 60°C) is almost impossible without heterogeneous surfaces (Baker and Kastner, 1981; Land, 1998; Roberts et al., 2013; Bosak and Newman, 2003), such as the surfaces of minerals (e.g., clays) (Liu et al., 2019) and biogenic materials (e.g., extracellular polymeric substances (EPSs)) (Petrash et al., 2017; Daye et al., 2019).

Laboratory and field research has shown that microorganisms can produce metabolites mediating the precipitation of dolomite at low temperature (Petrash et al., 2017; Sánchez-Román et al., 2008; Li et al., 2018; Daye et al., 2019; Warthmann et al., 2000). On these biogenic substances, carboxyl groups (R-COO⁻) serve as the nucleation sites for dolomite crystallization and stabilization (Roberts et al., 2013; Kenward et al., 2013; Liu et al., 2019; Wang et al., 2009; Paulo et al., 2020). Carboxyl-rich oxidative metabolites (CROMs) have been found abundant in the natural environments where dolomite heavily precipitates (Sánchez-Román et al., 2008; Krause et al., 2012; Brauchli et al., 2016; Diloreto et al., 2021). Moreover, it has been revealed that microbially mediated formation of dolomite occurs only when the concentration of carboxyl sites (i.e., the density of carboxyl groups on biogenic surfaces)

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exceeds a threshold that depends on the specific experimental/environmental conditions (Kenward et al., 2013; Liu et al., 2019). These observations suggest a strong positive correlation between CROMs and dolomite production under natural conditions.

Dolomite precipitation, however, not only links to Earth's carbon cycle; changes in the oxygen (O₂) concentration in seawater (Song et al., 2017; Song et al., 2019; Meyer and Kump, 2008; Wallace et al., 2017) also significantly influence dolomite formation (McKenzie and Vasconcelos, 2009; Diloreto et al., 2021). At geologic timescales, dolomite abundance, which is defined as the ratio of dolomite thickness to total carbonate thickness in carbonate successions, has been shown to negatively correlate with O₂ levels in Earth's atmosphere and oceans during the Phanerozoic (McKenzie and Vasconcelos, 2009; Negi et al., 1996; Li et al., 2021). However, the underlying mechanisms responsible for this negative correlation remain poorly understood. Moreover, Earth's oxygen and carbon cycles are highly coupled via photosynthetic activities and aerobic respiration (Berner, 2004; Arndt et al., 2013), which adds another layer of complexity to the dolomite problem.

Here I propose a mechanism linking the dolomite problem to the biogeochemical cycles of oxygen and carbon and offer an innovative interpretation of the significant difference in dolomite abundance during the Precambrian and Phanerozoic. I suggest that oxidative metabolisms have dichotomous effects on dolomite precipitation: low-O₂ environments promote CROM production and therefore favor dolomite production, while high-O₂ conditions inhibit CROM formation and thus impede dolomite formation. In modern environments, CROMs are produced by aerobic metabolisms that are catalyzed by oxidative enzymes (Findlay, 2021; Liang et al., 2018). In this study, I focus on a representative, CROM-producing enzyme family, Baeyer-Villiger mono-oxygenases (BVMOs) (Landry et al., 2017; Liang et al., 2018; Tolmie et al., 2019), and reconstruct their evolutionary history using phylogenetic methods. These analyses show that the evolution of BVMOs of microbial species in phyla Proteobacteria, Actinobacteria, and Chloroflexi, which have been shown to contribute to CROM production (Landry et al., 2017; Diloreto et al., 2021) and dolomite formation (Diloreto et al., 2021; Liu et al., 2019; Tang et al., 2012) in the modern environment, was temporally correlated with the variation in dolomite abundance on Earth's surface over geologic time.

2. Material and methods

2.1. Precambrian and Phanerozoic dolomite abundance and dissolved O₂

To reconstruct the time series of dolomite abundance on Earth's surface since the Archean to Phanerozoic, I first computed the mean value in each bin of 100 million years (Myr) for the compiled datasets of Precambrian (Cantine et al., 2020) and Phanerozoic (Li et al., 2021) dolomite abundance. I then calculated the moving averages of these mean values using a window of 300 Myr. This time interval (i.e., 300 Myr) is the uncertainty range (i.e., 95% confidence interval) of the age distributions in the Phanerozoic on the timetree of BVMO homologs (Section 2.3), which was used to reconstruct the diversification rates of BVMO genes over geologic time (Section 2.4). The time series of dolomite abundance and BVMO diversification rates are shown in Fig. 3(A). The concentration of dissolved O₂ in deep seawater since the Archean to Phanerozoic, which was adapted from Song et al. (2017), is presented in Fig. 3(B).

2.2. Species tree and gene tree reconstruction

The National Center for Biotechnology Information (NCBI), the Pathosystems Resource Integration Center (PATRIC), and the Integrated Microbial Genomes & Microbiomes (IMG) databases were used to search for the sequences of interest. Homologous ribosomal protein sequences from 298 taxa (Supplementary Information, Table S1) were used to reconstruct the species tree, and 330 homologous BVMO

sequences were used to reconstruct the gene tree. The MAFFT program (Katoh and Standley, 2013) with the progressive method "FFT-NS-2" and the score matrix "bl 62" (i.e., BLOSUM62) was applied to align the sequences. Alignments were then visualized on Clustal X (Larkin et al., 2007), and the poorly aligned regions were manually removed. The program SequenceMatrix (Vaidya et al., 2011) was used to concatenate the aligned ribosomal protein sequences.

The maximum-likelihood species tree and gene tree were inferred using IQ-TREE (version 1.6.3) (Nguyen et al., 2015) with the ultrafast bootstrap algorithm (Minh et al., 2013) and 100 replicates. It turned out that the "LG + I + R9" model (i.e., an LG model for amino-acid exchange rate matrices, invariable sites, and a Free Site Rate model with 9 categories of rates (Le and Gascuel, 2008; Soubrier et al., 2012)) best fits the concatenated ribosomal protein alignments, and the "LG + R6" model (i.e., an LG model for amino-acid exchange rate matrices and a Free Site Rate model with 6 categories of rates (Le and Gascuel, 2008; Soubrier et al., 2012)) best fits the BVMO protein alignments. The species tree was manually rooted so that Proteobacteria, Bacteroidetes, Ignivibacteria, and Chlorobi are grouped in one clade, while Actinobacteria, Chloroflexi, and Cyanobacteria are grouped in the other clade because previous studies have consistently supported this rooting of bacteria (Battistuzzi et al., 2004; Battistuzzi and Hedges, 2009). Due to the lack of knowledge about the root for the BVMO gene tree, I applied the minimal ancestor deviation method (Tria et al., 2017) to infer its root position.

2.3. Divergence time estimation for phylogenies

The program PhyloBayes (Version 4.1c) (Lartillot et al., 2009) with parameters "-catfix C60 -ugam -bd -sb -nchain 2 100 0.3 50" and all other parameters default was used to estimate the divergence time of the phylogenies. The times of the earliest evidence for Earth's habitability (i.e., 4.4 billion-year-old zircon) (Valley et al., 2014) and the oldest known bacterial microfossils (i.e., 3.4 billion-year-old stromatolites in the Warrawoona Group (Australia)) (Schopf, 1993) were set as the older and younger bounds, respectively, for the species tree root prior. Our belief in the true age of the species tree root becomes weaker as the date approaches these two bounds (i.e., 4.4 Ga and 3.4 Ga); therefore I applied a normally distributed root prior with a 95% confidence interval across these two bounds (i.e., a mean of 3.9 Ga and a standard deviation of 0.25 Ga). The uncorrelated gamma model (i.e., -ugam) (Drummond et al., 2006) was used for the relaxed molecular clock. Because it is very likely that the last universal common ancestor is deeper than the root node on the species tree (Weiss et al., 2016), a hard bound was imposed on the older bound for the species tree root prior. While it is unlikely that the 3.4 billion-year-old stromatolites represent stem bacterial diversity (Magnabosco et al., 2018), it remains a possibility; therefore I set a soft bound (Yang, 2014) on the younger age of the species tree root prior. The calibrations for other crown and stem nodes on the species tree, which were obtained in a previous study (Magnabosco et al., 2018), are provided in Table S2. These uniform age calibrations have broad ranges and thus are unlikely over-specifying due to biases from previous analyses.

To estimate the divergence time of BVMOs, the 95% confidence intervals for several nodes (Table S2) on the species tree, which have high bootstrap supports (> 90%) and are also present in the gene tree, were used as the secondary calibrations for the gene tree. Previous work has suggested that the diversification time of oxidative metabolisms and the timing of the Great Oxidation Event (GOE) should be consistent (Kim et al., 2012); however, to avoid the false precision caused by the lack of knowledge, I imposed a flat age interval of 3.2–1.2 Ga as the gene tree root prior. The older bound (i.e., 3.2 Ga) of this range corresponds to the published age estimates for the split between Cyanobacteria and non-photosynthetic lineages (Magnabosco et al., 2018), while the younger bound (i.e., 1.2 Ga) is sufficiently young to include the 95% confidence interval for the crown node ages of representative, CROM-producing

bacteria clades on the species tree.

2.4. Divergence rates

The “-readdiv” command in PhyloBayes (Lartillot et al., 2009) was used to generate the inferred timetrees of the phylogenies. The first 20% of sampled node ages were deleted to exclude the unconverged timetrees. The command “-v” in PhyloBayes was used to output all inferred timetrees. Diversification rates of the BVMO genes of phyla Actinobacteria, Chloroflexi, and Proteobacteria were calculated using their posterior ages. The per-gene diversification rate, r , in continuous time is defined by $r = \frac{1}{N} \frac{dN}{dt} = \frac{d \log N}{dt}$, where $N(t)$ is the number of nodes at time t . To compute r in discrete time, I denote N_i as the average number of nodes at time t_i , where the bin width $\Delta t = t_{i+1} - t_i$ equals 100 million years (Myr). The discrete diversification rate r_i at time $t_i + \Delta t/2$ is then expressed as $r_i = \frac{1}{\Delta t} \log \frac{N_{i+1}}{N_i}$.

3. Results

3.1. Carboxyl-rich oxidative metabolites

Carboxyl groups, which are a characteristic of many types of partially degraded organic matter produced by oxidative metabolisms (Wershaw, 1993; Rashid, 2012; Boye et al., 2017; Jinich et al., 2020), have been revealed to promote dolomite precipitation in modern natural ecosystems (Petrasch et al., 2017; Diloreto et al., 2021). As reactive, negatively-charged functional groups, carboxyls on oxidative metabolites elevate dolomite formation by increasing the loading of Ca^{2+} and Mg^{2+} ions onto heterogeneous surfaces (Qiu et al., 2017; Liu et al., 2019), or by enhancing the dehydration of Mg^{2+} - H_2O complexes via the metal-chelation (Roberts et al., 2013; Kenward et al., 2013) or adsorption-displacement (Liu et al., 2019; Zhang et al., 2015) mechanisms. These observations suggest that the incomplete degradation of organic matter in the presence of O_2 may raise the density of carboxyls on the surfaces of biogenic substances and therefore facilitate the formation of dolomite.

Fig. 1 provides a conceptual picture. In panel (A), oxidative metabolisms are inhibited under an anaerobic condition, resulting in a low density of carboxyls on organic substances and therefore minor production of dolomite. In panel (B), CROMs formed in a low- O_2 environment elevate the number of carboxyl groups, enhancing dolomite precipitation. In panel (C), high O_2 levels lead to more complete oxidation of CROMs and transform them to CO_2 ; consequently, the density of carboxyls declines and dolomite formation is impeded. The juxtaposition of panels (A), (B), and (C) suggests that O_2 -limiting aerobic

environments are optimal for dolomite production.

3.2. Dichotomous effects of oxidative metabolisms on dolomite formation

To better understand how the coupled oxygen and carbon cycles influence the production of CROMs and therefore dolomite, I construct a simple model that considers only two types of organic matter: an “unoxidized” component (x) that can be readily degraded and a “partially-oxidized” component (y) that is transformed from x by oxidative metabolisms (Supplementary Information, Fig. S1). Complete oxidation of x and y yields CO_2 (z) as the end product. I assume that x and y are oxidized to z with rate constants k_1 and k_2 , respectively, where $k_2 < k_1$ because intermediate-stage metabolic products reward less energy to microbial metabolisms (Arndt et al., 2013; Shang, 2023). I denote the rate constant for the transformation from x to y as k_T . The degradation rates of x and y and the production rate of CO_2 at time t are then expressed in terms of the first-order kinetics (Arndt et al., 2013; Middelburg, 1989):

$$\frac{dx}{dt} = -(k_1 + k_T)x, \quad t \geq 0 \quad (1)$$

$$\frac{dy}{dt} = k_T x - k_2 y, \quad 0 \leq t \leq t_{\text{ox}} \quad (2)$$

$$\frac{dz}{dt} = k_1 x + k_2 y, \quad t \geq 0 \quad (3)$$

where t_{ox} , also called *oxygen exposure time* (Hedges and Keil, 1995; Hartnett et al., 1998), is the length of time that organic matter is exposed to O_2 . I assume that the initial amount of CO_2 is 0, and denote the initial total amount of organic carbon by $a = x(0) + y(0)$ and the initial fraction of y by f . The initial conditions then read

$$x(0) = a(1 - f), \quad y(0) = af, \quad \text{and} \quad z(0) = 0. \quad (4)$$

For the sake of simplicity, I introduce dimensionless rate constants $\kappa_T = k_T/k_1$, $\kappa_2 = k_2/k_1$, and dimensionless time $\tau = k_1 t$. The analytic solutions to the dimensionless form of Eqs. (1)–(3) are provided in Supplementary Information, Section S1.

As discussed in Section 3.1, carboxyl groups are a characteristic of partially oxidized organic matter produced by oxidative metabolisms; here, I identify the y component as CROMs. Partially oxidized organic compounds are highly heterogeneous (Arndt et al., 2013; Shang, 2023), so I calculate the average amount $\langle y \rangle$ (Supplementary Information, Section S2), where $\langle \cdot \rangle$ represents of the average of a quantity. Because the transformation of x to y by oxidative metabolisms occurs in the presence of O_2 , the production of y ceases when O_2 is completely

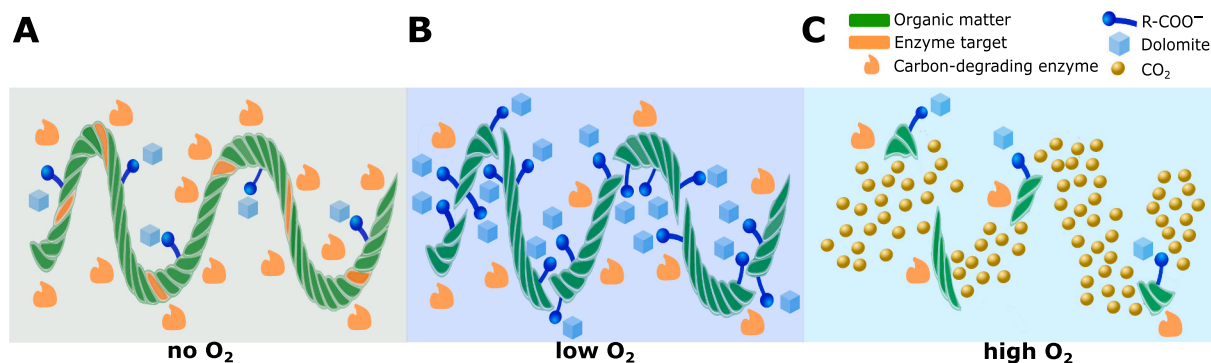


Fig. 1. Dolomite precipitation mediated by carboxyl-bearing biogenic substances in anaerobic, low- O_2 , and high- O_2 environments. (A) The low density of carboxyl groups (i.e., R-COO^-) on the biopolymer that has not been processed by oxidative metabolisms limits the formation of dolomite. (B) Carboxyl groups are formed by oxidative enzymes in a low- O_2 environment. These carboxyl groups on the partially oxidized organic substances increase the number of nucleation sites for dolomite crystallization and stabilization, enhancing the precipitation of dolomite. (C) Further oxidation under a high- O_2 condition transforms the partially oxidized, carboxyl-rich organic substances to CO_2 , which decreases the density of carboxyl groups and therefore reduces the production of dolomite.

consumed or when organic matter is transported/sequestered into O_2 -free environments; this implies that $\kappa_T = 0$ when $\tau > \tau_{ox}$ (i.e., $\kappa_T = 0$ when $t > t_{ox}$ in their dimensional forms). Compared to the unoxidized portion, the partially oxidized component generally is less energetically rewarding to microorganisms and therefore is much more recalcitrant (Arndt et al., 2013; Shang, 2023). Consequently, its degradation usually is rather slow and even stops in the absence of O_2 (Hedges and Keil, 1995; Arndt et al., 2013; Shang, 2023). Hence I assume that $\kappa_2 \approx 0$ when $\tau > \tau_{ox}$; therefore, $\langle y(\tau_{ox}) \rangle$ is the portion responsible for dolomite production in the system of Eqs. (1)–(3).

The change of $\langle y(\tau_{ox}) \rangle$ with τ_{ox} depends on two parameters: κ_T^* and τ_{ox}^* , which represent the critical values of κ_T and τ_{ox} , respectively. Mathematical expressions of these two parameters and the relevant analyses are presented in Supplementary Information, Section S2. Fig. 2(A) shows theoretical predictions for the variations of $\langle y(\tau_{ox}) \rangle$ with τ_{ox} when $\kappa_T > \kappa_T^*$ (blue curve) and $\kappa_T < \kappa_T^*$ (red curve). If $\kappa_T > \kappa_T^*$, then an increase in τ_{ox} elevates CROM production when $\tau_{ox} < \tau_{ox}^*$ but reduces CROM formation when $\tau_{ox} > \tau_{ox}^*$. However, if $\kappa_T < \kappa_T^*$, CROM production monotonically decreases with τ_{ox} . The inequalities $\kappa_T > \kappa_T^*$ and $\kappa_T < \kappa_T^*$ are expected to be satisfied in O_2 -limiting and -rich environments, respectively; the reasoning for this is discussed in Supplementary Information, Section S2. Meanwhile, low and high levels of dissolved O_2 in seawater correspond to short and long τ_{ox} , respectively; therefore, the solid segments in Fig. 2(A) represent predictions for realistic situations while the dashed segments in Fig. 2(A) are purely theoretical and not expected to occur.

As discussed above, dolomite precipitation and dissolved O_2 in seawater are positively correlated with $\langle y(\tau_{ox}) \rangle$ and t_{ox} , respectively. Therefore, the relation between $\langle y(\tau_{ox}) \rangle$ with t_{ox} (Fig. 2(A)) can be converted to the relation between dolomite production and dissolved O_2 (Fig. 2(B)). By combining theoretical predictions for realistic cases (i.e., the solid blue and red segments in Fig. 2(A)), Fig. 2(B) illustrates the dichotomous effects of oxidative metabolisms on dolomite production under low and high O_2 levels. In O_2 -limiting environments, where $\kappa_T > \kappa_T^*$ and $\tau_{ox} < \tau_{ox}^*$ are expected to widely hold (Supplementary Information, Section S2), CROM formation and therefore dolomite precipitation are facilitated (blue segment in Fig. 2(B)); an increase in dissolved O_2 would promote dolomite production. In contrast, O_2 -rich conditions, under which $\kappa_T < \kappa_T^*$ and $\tau_{ox} > \tau_{ox}^*$ should be generally satisfied (Supplementary Information, Section S2), enhance the transformation of CROMs to CO_2 and thus inhibit dolomite formation (red segment in Fig. 2(B)); a higher concentration of dissolved O_2 in this regime would lead to less precipitation of dolomite.

The above CROM hypothesis suggests dichotomous effects (i.e.,

facilitation and inhibition) of oxidative metabolisms on dolomite formation under low- and high- O_2 conditions. These theoretical predictions provide a plausible interpretation of the dolomite problem, wherein dolomite was abundant in ancient O_2 -limiting environments but is rare in modern O_2 -rich ecosystems. However, did the CROM-producing oxidative metabolisms exist on the ancient Earth, and was their evolution temporally correlated with the variation in dolomite abundance at the geologic timescale? The next section addresses these questions.

3.3. Dolomite abundance and CROM-producing gene diversification

Whether the mechanisms suggested here were responsible for the massive production of dolomite on the ancient Earth hinges on the existence of CROM-producing oxidative metabolisms in deep time. Microbial species in phyla Proteobacteria, Actinobacteria, and Chloroflexi, which have a very ancient origin among the earliest bacterial lineages (Woese et al., 1990; Hug et al., 2016) and are prevalent in a variety of the modern environments (Mehrshad et al., 2018; Morris et al., 2004; Liu et al., 2019), have been shown to contribute to CROM production (Landry et al., 2017; Diloreto et al., 2021) and dolomite precipitation (Diloreto et al., 2021; Liu et al., 2019; Tang et al., 2012). Laboratory and field studies (Landry et al., 2017; Liu et al., 2020) have revealed that the BVMOs, a group of oxygenases involved in the oxidation of a wide range of substrates (Liang et al., 2018; Tolmie et al., 2019), play a key role in the CROM-producing oxidative metabolisms of these phyla. In the presence of O_2 , BVMOs can insert O atoms from O_2 into organic carbon chains to form carboxyl groups in marine environments (Liang et al., 2018; Landry et al., 2017). Therefore, reconstructing the evolutionary history of BVMOs using phylogenetic methods may offer an avenue to test the CROM hypothesis.

To infer the divergence of BVMO genes in phyla Proteobacteria, Actinobacteria, and Chloroflexi, I reconstructed a species tree for 298 taxa and a gene tree for 330 BVMO sequences of these taxa. The molecular clock technique (Ho and Duchêne, 2014; Yang, 2014) was applied to estimate the diversification time of the ancestral species and BVMO genes on the reconstructed phylogenies. Details on sequence datasets, phylogenetic reconstruction, and molecular clock calibrations are provided in Section 2 and Supplementary Information, Tables S1–S2. The reconstructed maximum-likelihood phylogenies and inferred timetrees are presented in Supplementary Information, Figs. S2–S5.

The timetree of BVMO homologs of the species within phyla Actinobacteria, Chloroflexi, and Proteobacteria (Supplementary Information, Fig. S5) shows that BVMO genes diversified at rates that varied non-uniformly along time. The diversification rate of O_2 -utilizing BVMOs is expected to be correlated with the redox state of seawater and therefore

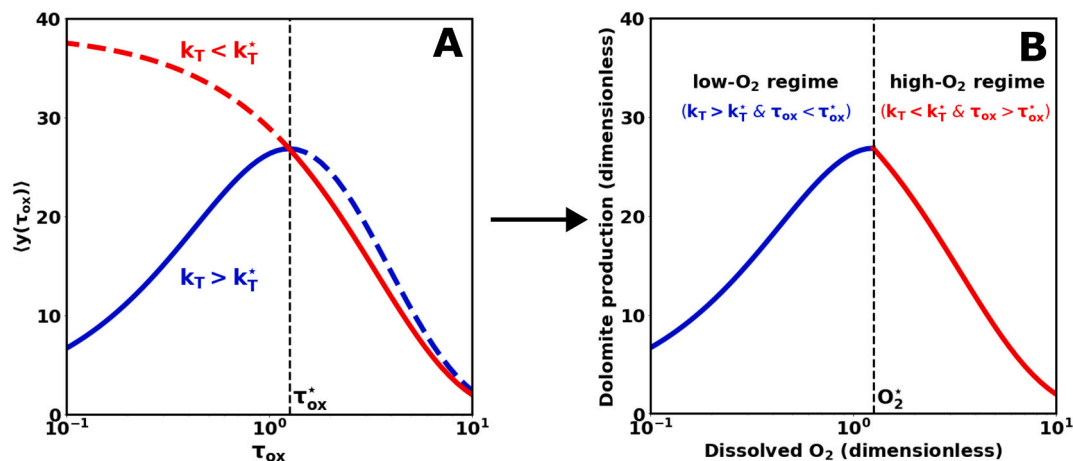


Fig. 2. (A) A theoretical prediction for the effects of oxygen exposure time (τ_{ox}) on CROM formation ($\langle y(\tau_{ox}) \rangle$) when $\kappa_T > \kappa_T^*$ (blue) and $\kappa_T < \kappa_T^*$ (red). The vertical dashed line represents $\tau_{ox} = \tau_{ox}^*$. (B) Dichotomous effects of oxidative metabolisms on dolomite production in low and high regimes of dissolved O_2 in seawater.

serves as a biological proxy for dissolved O_2 concentration and thus dolomite precipitation. In an O_2 -limiting environment, which favors dolomite formation (Fig. 1(B)), a rise in the dissolved O_2 concentration should lead BVMO genes to disperse into wider, oxygenated niches in oceans, resulting in more production of CROMs and therefore dolomite. In contrast, under an O_2 -rich condition that inhibits dolomite production (Fig. 1(C)), although BVMO genes would further diversify and spread as the oceanic environment becomes more oxygenated, high levels of O_2 would result in complete oxidation of CROMs to CO_2 , reducing dolomite precipitation.

To test the above speculations, I reconstructed dolomite abundance on Earth's surface (blue curve in Fig. 3(A)) and calculated the diversification rates of BVMO genes (red curve in Fig. 3(A)) using the data compiled by Li et al. (2021) and Cantine et al. (2020) (Section 2.1) and the age information in the posterior timetrees (Section 2.4), respectively. Fig. 3(A) illustrates that the abundance of dolomite basically remained high across the Precambrian before it dramatically decreased to the prolonged, low levels during the Phanerozoic. On the other hand, four periods of rapid diversification appear in the time series for BVMO genes (Fig. 3(A)): ~2500 Ma (i.e., the Late Neoproterozoic/Early Paleoproterozoic), ~1100 Ma (i.e., the Middle/Late Mesoproterozoic), ~600 Ma (i.e., the Late Neoproterozoic/Early Paleozoic), and ~400–300 Ma (i.e., the Middle/Late Paleozoic). Fig. 3(B), which is adapted from Song et al. (2017), shows the evolution of the redox state (i.e., dissolved O_2 concentration) of seawater over geologic time. The four time intervals of rapid diversification of BVMOs correspond to four significant events in the evolution of Earth's oxygen cycle: the GOE (Lyons et al., 2014; Canfield, 2014), the divergence of red and green algae (Sánchez-Baracaldo et al., 2017; Knoll et al., 2006), the Late Neoproterozoic Oxidation Event (NOE) (Lyons et al., 2014; Canfield, 2014), and the Permo-Carboniferous O_2 pulse (Bernier, 2004; Beerling and Bernier, 2000). Moreover, the diversification rate of BVMO genes significantly declined between 800 and 600 Ma (Fig. 3(B)), during which the Neoproterozoic global glaciation events occurred (Hoffman et al., 1998; Hoffman et al., 2017).

4. Discussion

The CROM hypothesis proposes dichotomous effects of oxidative metabolisms on dolomite formation in different regimes of O_2 concentrations. Oxygen-utilizing enzymes, such as those CROM-producing oxygenases, would have become more diverse as Earth evolved toward a more oxygenated world. Thus, variations in dolomite abundance should have been temporally correlated with the ecological diversifications of oxidative metabolisms along geologic time.

In the Neoproterozoic, the early whiffs of O_2 (Ostrander et al., 2021) probably had initiated the evolution of oxidative metabolisms (Taverne et al., 2020), such as the CROM-producing pathways. This speculation is supported by the early divergence of BVMO genes in different microbial lineages (Supplementary Information, Figs. S4 and S5). BVMO genes might have started to diversify in this O_2 -limiting world, facilitating the formation of dolomite (Fig. 3(A)). With the rapid accumulation of O_2 in the GOE, Earth's surface became oxygenated but the concentration of dissolved O_2 in seawater remained low (Lyons et al., 2014; Canfield, 2014). This low-level steady state of atmospheric O_2 likely lasted for almost two billion years (Fig. 3(B)) (Lyons et al., 2014; Canfield, 2014), resulting in slow or even stagnant diversification of BVMO genes (Fig. 3(A)). In the meantime, the protracted O_2 -limiting environments would have favored CROM production and therefore dolomite precipitation, leading to the generally high abundance of dolomite in the Proterozoic sedimentary records (Fig. 3(A)).

The more oxygenated environment (Lyons et al., 2014; Canfield, 2014) in the Phanerozoic (Fig. 3(B)) might have fueled the diversification of BVMO genes (Fig. 3(A)). In particular, the diversification rate reached a maximum in the Permo-Carboniferous period (Fig. 3(A)), during which the atmospheric O_2 rose to extraordinarily high levels (Bernier, 2004; Beerling and Bernier, 2000). In this environment, most of organic matter arriving in oceans and sediments would have been completely transformed to CO_2 , reducing CROM formation and thus dolomite precipitation. Consequently, dolomite abundance on Earth's surface dramatically declined and eventually attained and remained at

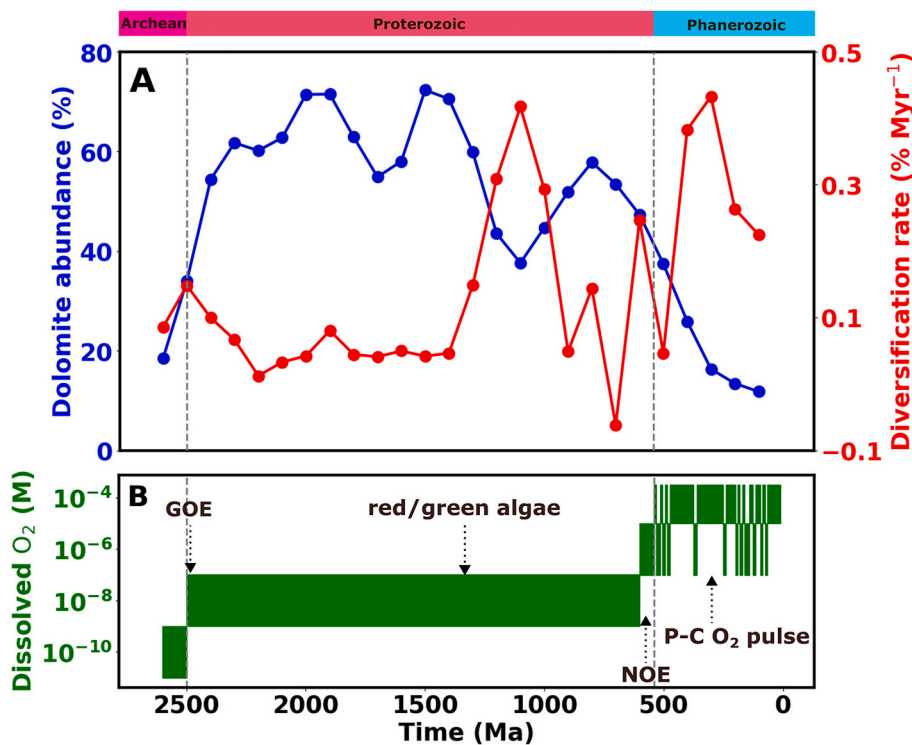


Fig. 3. (A) The variation in dolomite abundance on Earth's surface (blue) and the diversification rates of BVMO genes in phyla Proteobacteria, Actinobacteria, and Chloroflexi (red) over geologic time (unit: millions of years ago (Ma)). The two vertical dashed lines represent the Archean/Proterozoic and Proterozoic/Phanerozoic boundaries. To reconstruct dolomite abundance, I calculated the mean value in each bin of 100 million years (Myr) for the data compiled in Li et al. (2021) and Cantine et al. (2020), and then computed the moving averages of these mean values using a window of 300 Myr. This period of 300 Myr is the uncertainty range (i.e., 95% confidence interval) of the age distributions in the Phanerozoic on the timetree of BVMO homologs (Supplementary Information, Fig. S5). In the time series of BVMO diversification rates, four intervals of fast diversification appear: the Late Neoproterozoic/Early Paleoproterozoic (~2500 Ma), the Late Mesoproterozoic (~1100 Ma), the Late Neoproterozoic/Early Paleozoic (~600 Ma), and the Middle/Late Paleozoic (~400–300 Ma). (B) The evolution of the dissolved O_2 concentration in seawater (unit: molar (M)) over geologic time (adapted from Song et al., 2017). The four time intervals witnessed rapid diversification of BVMOs in (A) correspond to four significant events in the history of Earth's oxygen cycle: the GOE (Lyons et al., 2014; Canfield, 2014), the rapid divergence of red and green algae (Sánchez-Baracaldo et al., 2017; Knoll et al., 2006), the NOE (Lyons et al., 2014; Canfield, 2014), and the Permo-Carboniferous (P-C) O_2 pulse (Bernier, 2004; Beerling and Bernier, 2000).

low levels throughout the Phanerozoic O₂-rich environments (Fig. 3(A)).

Fig. 3(A) also shows rapid diversification of BVMO genes and a drop in dolomite abundance in the Middle/Late Mesoproterozoic. The increased production of O₂ by the oxygenic photosynthesis of red and green algae during this period probably elevated the atmospheric O₂ concentration (Knoll et al., 2006; Sánchez-Baracaldo et al., 2017), resulting in fast diversification of BVMO genes. On the other hand, the relatively high O₂ level might have reduced the formation of CROMs and inhibited dolomite production. The fast, Mesoproterozoic diversification of BVMO genes was followed by a remarkable decline around 700 Ma (Fig. 3(A)). This drop might have been a consequence of the Neoproterozoic global glaciation events, during which massive ice shelves inhibited oxygenic photosynthesis and therefore reduced O₂ production (Hoffman et al., 1998; Hoffman et al., 2017). Such O₂-limiting environments again likely favored the formation of CROMs; however, the synchronous decline in the production of organic compounds, which serve as enzyme substrates, would have curtailed the enhancement of dolomite formation. Consequently, although the Neoproterozoic might have witnessed an increase in dolomite precipitation, this rise is likely to have achieved a lower peak than those during the Paleoproterozoic and Mesoproterozoic (Fig. 3(A)).

The phylogenetic analyses above provide plausible results; future investigations, however, are required to further validate the CROM hypothesis. First, the temporal precision that can be achieved using molecular clock techniques is limited by the single family of BVMO genes; studying the evolutionary history of other O₂-utilizing and CROM-producing enzyme families potentially offers extra support for the theory presented in this work. Furthermore, laboratory experiments on the influence of oxidative metabolisms on the formation of CROMs and dolomite under conditions analogous to Earth's ancient O₂-limiting environments could provide valuable tests for the CROM hypothesis. In addition, the model in this study focuses on the effects of O₂ on dolomite formation via promoting/inhibiting CROM production but does not consider other physical and chemical factors, such as temperature, pH, alkalinity, and Mg/Ca ratio (Baker and Kastner, 1981); integrating these variables into the theoretical framework here may offer a more comprehensive understanding of the mechanisms responsible for the dolomite problem.

The CROM hypothesis suggests several approaches for further investigation of the dolomite problem as well. Some anaerobic microorganisms, such as sulfate-reducing bacteria, have been shown to produce carboxyl-rich EPSs, mediating the nucleation and stabilization of dolomite (Krause et al., 2012; Petrash et al., 2017). The abundance of electron acceptors (e.g., SO₄²⁻) utilized by these microbial species would rise with O₂ concentration via the oxidation of their reduced-state couples (e.g., H₂S). Investigating whether and how such increases in the abundance of weaker electron acceptors with dissolved O₂ concentrations influence the production of EPSs and therefore dolomite would provide more insights into the dolomite problem. Moreover, studies on the biological aspect of dolomite precipitation and the dolomite problem, including the present work, generally focus on microbial metabolisms (Sánchez-Román et al., 2008; Liu et al., 2019; Daye et al., 2019; Kenward et al., 2013; Krause et al., 2012; Petrash et al., 2017); the correlation between the macroevolution of life and the abundance of dolomite has rarely been studied. Dramatic variations of biomass, especially during life explosions and extinctions, might have led to significant changes in delivery rates of organic matter into the ocean and sediments, alternating the production rates of CROMs and thus dolomite. Future research in this direction may offer a new perspective for deciphering the dolomite problem. Additionally, previous research has proposed two distinct views on the dolomite problem with respect to diagenetic stages: early-diagenetic (Chang et al., 2020) and burial-hydrothermal (Gregg et al., 2015) dolomitization. The former suggests that specific seawater conditions in the Precambrian were responsible for the intensive precipitation of dolomite at Earth surface

temperatures (lower than 60°C) during the early diagenesis (Chang et al., 2020), while the latter proposes that the large volume of dolomite in the Precambrian sedimentary records derived from the dolomitization of calcite or aragonite precursors at temperatures higher than 100°C (Gregg et al., 2015). The CROM hypothesis does not disprove the burial-hydrothermal dolomitization, but it suggests an early diagenetic mechanism that might have contributed to the variation in dolomite abundance over geologic time. Future measurements of the abundance of dolomite in deep time with meticulous identification of its origin (i.e., early-diagenesis or burial-hydrothermal dolomitization) would provide more reliable evidence to support or falsify the CROM hypothesis and other previous hypotheses.

In summary, the CROM hypothesis offers a resolution for the dolomite problem via linking the evolution of Earth's oxygen cycle to the dolomite abundance in sedimentary records and predicts the dichotomous effects of oxidative metabolisms on dolomite formation under different O₂ levels. The temporal correlation between the variation in dolomite abundance on Earth's surface and the evolution of a representative, CROM-producing oxidative enzyme family supports the theory. The complexity of biogeochemical cycles suggests that a similar co-evolution of microorganisms and the environment probably helps interpret the temporal and spatial heterogeneity of geologic records on Earth (e.g., banded iron formations (Klein, 2005)) and potentially provides insights into the evolution of dolomite on exoplanets (Bosak et al., 2021; Horgan et al., 2020).

Author contributions

H. Shang conceived the project, performed the research, and wrote the manuscript.

Declaration of Competing Interest

The author declares no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data needed to evaluate the conclusions in the paper are presented in the main text and Supplementary Information.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.gloplacha.2023.104041>.

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