Dolomite - A link to Phanerozoic ocean conditions.

Abstract

A literature study was conducted on the present standings of what is known as "the dolomite problem"; a geological enigma which has puzzled geologists for more than a century and the experimental precipitation studies which attempt to address the lack of knowledge surrounding this enigmatic mineral. The dolomite problem concerns the abundance of ancient dolomite throughout the Phanerozoic rock record hosted in carbonate platforms vs. the scarcity of modern dolomite formation in marine environments. Unravelling the mysteries of dolomite formation requires a better understanding of the conditions under which dolomite forms and the rate of precipitation under those conditions. Better understanding this phenomenon has important implications to palaeo-environmental studies as it provides a link to the evolution of Earth's ocean chemistry.

Introduction

Dolomite ($CaMg(CO_3)_2$) is one of the most abundant carbonate minerals in the geological record [1] and is the most oversaturated carbonate mineral of the modern ocean [2] Although the ocean is highly oversaturated in respect to dolomite, the mineral rarely forms in modern environmental systems [3,4]. In most ancient dolomite units, the dolomite often constitutes more than 90% of the mineralogy, often overprinting entire limestone platforms as diagenetic units that are typically hundreds of meters thick and can extend across areas over one hundred kilometres wide, in contrast Holocene dolomites comprise units that are seldom over a meter thick, dolomite constitutes less than 50% of the mineralogy and forms in patches across areas only several kilometres wide [5]. Dolomite is formed by two major mechanisms in the natural environment: (i) "primary dolomite", directly from solution as a precipitate and (ii) "secondary dolomite" formed by burial or diagenesis, most commonly by secondary replacement (dolomitization) of a precursor aragonite or calcite [1,4,6–8]. The largest dolomite deposits in the geological record were formed throughout the Phanerozoic and are diagenetic in origin, i.e. secondary dolomites [1,4']. In modern environments however, dolomites form through the direct precipitation of primary dolomite in a small number of hypersaline environments such as evaporitic lakes or sabkhas [10–16]. In these modern hypersaline settings, microbial metabolic processes of dominantly sulfate reduction or methanogenesis cause increased alkalinity which together with high Mg:Ca concentrations (1:1 – 100:1) produces high supersaturation levels in respect to dolomite which commonly leads to formation of dumbbell-shaped dolomite aggregates [17–19]. The transition from dominantly indirect secondary dolomite formation through dolomitization of calcite / aragonite to the direct formation of dolomite through precipitation is widely agreed upon to be related dominantly to changes in the chemical environment of the ocean throughout geologic time [1,5,7,9,20]. The vast occurrence of dolomite throughout the Phanerozoic vs. the paucity of dolomite formation in modern systems is known as the "dolomite problem", solving this problem requires knowledge of the conditions under which the mineral forms and the rate of precipitation under these conditions. There are strong arguments throughout literature which argue the most important control on dolomite formation is kinetics and that there simply has not been enough time to form extensive areas of secondary dolomite within the Holocene [5,21–23]. There is also the question of parity; do variations in ocean chemistry influence dolomite volumes in carbonate platforms? or do changes in the volume of dolomite influence ocean chemistry? Were times of widespread platform growth also times of widespread dolomitization? It has been argued that the levels of Mg in the ocean have remained relatively stable but changes in the rate of seafloor spreading have changed the levels of Ca in the ocean and hence effected the dominant dolomite mineralogies [24,25]. A

contrasting argument is that the abundance of $MgSO_4$-depleted evaporites in the Cretaceous may reflect a substantial episode of carbonate platform growth and dolomitization in which case the dolomite formation has altered the ocean chemistry [26]. Another study argues that the relative level of Mg:Ca and pCO$_2$ of the dolomite precipitating fluid is substantially less important than the levels of oceanic oxygen controlling the intensity of anaerobic bacterial metabolism[8].

To put the dolomite problem simply; with our current understanding of dolomite formation we do not know, (1) why there is so much ancient dolomite and so little modern dolomite, (2) how the chemistry of ancient dolomite forming settings has changed over time, (3) how the volume of dolomite precipitation has altered through time, (4) the importance of kinetics vs. parity, (5) if dolomite formation controls ocean chemistry or if it's controlled by it and (6) what the effect of bacterial mediation is. Understanding the mechanisms of dolomite formation and unravelling the dolomite problem has been a goal of geologists worldwide for over a century which has important mineralogical and palaeo-environmental implications as it links the formation of dolomite with the long term evolution of Earth's ocean chemistry.

Equilibrium and kinetics in dolomite precipitation

Precipitating dolomite from any water source requires the following reaction to take place:

$$Ca^{2+} + Mg^{2+} + 2(CO_3^{2-}) = CaMg(CO_3)_2$$

which gives an equilibrium constant K defined by:

$$K = ([Ca^{2+}][Mg^{2+}][CO_3^{2-}]^2)/[CaMg(CO_3)_2]$$

Where [X] is the activity of the dissolved solid species.

The value of K is not currently known with any precision due to the difficulty of synthesizing dolomite at low temperatures, however estimates from modern, metastable dolomites and other lines of evidence have placed the value as $K \approx 10^{-16.5} - 10^{-17}$ [5,27,28]. By using the approximate activities of Ca^{2+}, Mg^{2+} and CO_3 in seawater an ion activity product (IAP) of the order $10^{-15.01}$ is given, indicating modern oceans are supersaturated with respect to dolomite by one to two orders of magnitude however dolomite is a rare precipitate in ocean waters. This strongly supports the contention that reaction kinetics are a dominant control in the precipitation of dolomite from modern ocean water [5]. The same argument can be made for secondary dolomite formation through the dolomitization of limestone platforms by modern seawater where the required reaction is as follows:

$$2CaCO_3 + Mg^{2+} = CaMg(CO_3)_2 + Ca^{2+}$$
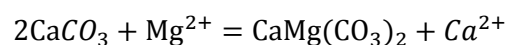
By taking the activity of the solid phases into account the equilibrium constant expression is expressed:

$$K = [Mg^{2+}]/[Ca^{2+}] = 0.67$$

Indicating the equation should go to the right when $[Mg^{2+}]/[Ca^{2+}] > 0.67$. Modern ocean water has a molar Mg/Ca ratio of approximately 5.2 and should not just precipitate dolomite but also be capable of dolomitizing limestone. This again is a strong argument for the reaction kinetic control on dolomitization [5].

Dolomite composition and lattice structure

The term dolomite does not refer to a mineral with a definitive chemical composition and lattice structure, however a compositional series which also exhibits subtle variations in the atomic arrangement within the crystal lattice[21,27–29]. Ideal dolomite refers to dolomite with a crystal lattice consisting of alternating layers of Ca and Mg, separated by layers of CO_3 that contains equal parts

magnesium and calcium represented by the chemical formula $CaMg(CO_3)_2$ *(Figure 1A)*. Very few natural sedimentary dolomites however are truly stoichiometric and are best represented as $Ca_{(1+x)}Mg_{(1-x)}(CO_3)_2$ with documented compositions ranging from $Ca_{1.16}Mg_{0.84}(CO_3)_2$ (calcian-dolomite) to $Ca_{0.96}Mg_{1.06}(CO_3)_2$ (magnesian-dolomite)[5]. Studies conducted by Lippmann (1973, 1982) showed that supersaturated seawater with respect to dolomite can persist for long periods of time without dolomite being precipitated, he argued that this reflects the relative strength of the electrostatic bond of the magnesium ion to water (>20% than that of Ca and much greater for CO_3)[31,32]. Lippmann concluded that although there was supersaturation with respect to dolomite, that the carbonate ions cannot overcome the hydration shell to bond with the Mg^{2+} *(Figure 1B)*. With Mg^{2+} effectively excluded from further reacting the main carbonate precipitate from modern seawater is aragonite. Higher Mg concentrations of hypersaline waters where we see modern precipitation of dolomite mean that the hydration barrier of magnesium is more easily overcome, however is still difficult to arrange into the mono-layers necessary to precipitate ideal, super-structured and stoichiometric dolomite. Lippmann argues that this is why highly disordered calcian-dolomite is the dominant form in most modern hypersaline setting and that to overcome the kinetic barrier it may be necessary for the seawater to be concentrated, heated, cooled, diluted and have its sulfate levels reduced or otherwise its activated CO_3^{2-} increased [31].
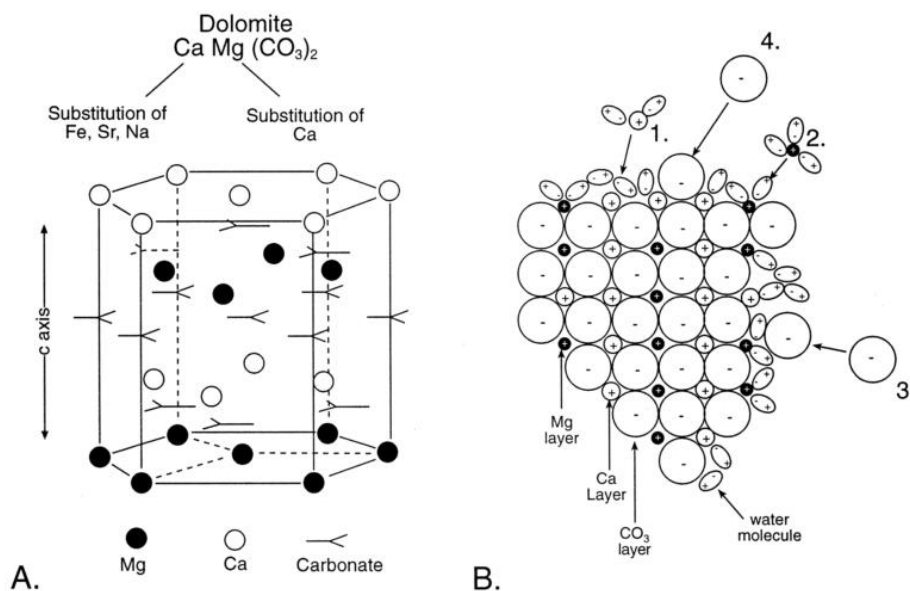

Figure 1. Dolomite lattice structure. (A) Ideal structure of dolomite with equal parts Mg:Ca (stoichiometric) in alternating layers of the crystal lattice separated by layers of CO$_3$. (B) Schematic of a non-ideal lattice structure of dolomite, showing how water molecules are preferentially bonded to cations on the surface of the growing crystallite. Because of the Ca ions are not as strongly hydrated as the Mg ions they tend to be incorporated in the Mg later, creating a typical calcian dolomite. Warren J (2000)

Each different dolomite mineral displays distinct thermochemical properties depending on the degree of lattice ordering and stoichiometry. There is a free energy difference which can be greater than 1.3 kcal/mol between ordered- and disordered- dolomite at Earth surface conditions. Completely disordered dolomite, termed "protodolomite" is the least stable and most soluble phase of dolomite and also the easiest to precipitate at Earth surface temperatures. Variability in the free energy and solubility of different dolomite phases means that dolomite precipitated in surface waters has a potential to recrystallize over time as it reorganizes its composition and structure to a more stable phase [21,27,33]. It is argued that because all non-stoichiometric, disordered dolomite is metastable, there must be a trend of burial diagenesis towards stoichiometry and lattice ordering [34].

Laboratory precipitation experiments

One of the major issues with studying dolomite experimentally is that it has been shown to be seemingly impossible to dolomitize calcium carbonates at Earth surface temperatures on a laboratory timescale [5,7,9,22]. High temperature experiments on the synthesis of dolomite from the dolomitization of calcite and aragonite can be difficult to extrapolate back to low, Earth-surface temperatures. Bullen and Sibley (1984) however showed that the micro-textures observed on a variety of fossils dolomitized at high temperatures in the laboratory were the same as the micro-textures observed in many natural samples [35]. Work by Kaczmarek and Sibley (2007) further demonstrated that natural and high-temperature synthetic crystals of dolomite were characterized by the same growth and dissolution features over a wide range of formation conditions and growth rates [36]. The study contends that high-temperature synthetic dolomite and low-temperature natural dolomite have the same crystal growth mechanisms and implies that results obtained from high-temperature synthesis experiments can be extrapolated and applied to low-temperature systems.

Evolution of stoichiometry and cation order

Studies by (Malone et al 1996) showed at 50-200°C and over long periods of time that proto-dolomite transforms to crystalline dolomite via a dissolution and re-precipitation reaction. This transformation lead to dolomite crystals with well-developed crystallographic faces, but significant crystallographic ordering of the Ca and Mg was only achieved at 200°C [37]. A recent study by Kaczmarek and Sibley (2011) which explored high temperature dolomitization of calcite in Mg-Ca-Cl solutions with various Mg:Ca ratios at a temperature of 218°C concluded several interesting results. The study determined that the dolomite composition and cation ordering within the crystal lattice both evolved independently as a function of reaction time. The study further showed that the rate of calcite replacement and the composition of the dolomite throughout the reaction were strongly dependent on the initial Mg:Ca ratio of the solution. Experiments that were run with lower Mg:Ca ratios were less stoichiometric (more Ca-rich) and the dolomitization progressed at slower rates, increased Mg:Ca in the initial solutions resulted in increased stoichiometry and faster reactions speeds. In all of the experiments dolomite composition remained relatively constant throughout most of the reaction process despite the chemistry of solution constantly evolving to lower Mg:Ca as magnesium was captured from and calcium was liberated into the solution with the transformation of calcite to dolomite. Despite dolomite composition remaining relatively constant, cation ordering within the crystal lattice increased with the percentage of dolomitized calcite (ie. the dolomite to calcite ratio). Stoichiometry of the dolomite was found to rapidly increase shortly before complete consumption of the reactants when >95% of the calcian reactants had been replaced by dolomite. After all the calcite reactants had been consumed the dolomite in each experiment became completely stoichiometric regardless of the initial Mg:Ca and the degree of cation order continued to increase with further reaction time. Results of this study suggest that natural dolomite does not simply evolve toward more stoichiometric compositions as the dolomite percentage in the rock increases (ie. with further reaction progress), rather that carbonate rocks with higher dolomite to limestone ratios have underwent dolomitization in solutions with higher Mg:Ca which results in more stoichiometric dolomite and faster reaction progress which allows a greater percentage of the rock to be dolomitized [38]. A more recent high temperature dolomitization study by Weiqiang et al. (2015) treated calcite and aragonite seeds in high Mg:Ca solutions at temperatures of 130, 160 and 220 °C. The study showed that the morphology of the synthesized dolomite was dependant on the starting mineralogy suggesting a strong control of the carbonate precursor on the pathway of dolomitization. Synthesis experiments with calcite as the seed material produced aggregates of dolomite which retained the 5-20µm rhombohedral morphology of the original calcite crystals,

however contained numerous sub-micron sized cavities. The dolomite inheriting the original calcite morphology implies that the dolomite was formed via a mineral replacement reaction, this is likely due to calcite and Mg-bearing calcite sharing a common lattice configuration with dolomite despite a small difference in the unit cell volumes [39], and thus facilitating cation replacement of Ca^{2+} by Mg^{2+} to cause dolomitization of the calcite. The smaller unit cell volume of dolomite relative to that of calcite causes the mineral to shrink during the replacement reaction and produces the aforementioned submicron-sized cavities [40]. Synthesis experiments beginning with the aragonite precursor typically produced fine-grained (1-5μm) well dispersed, euhedral rhombohedrons of dolomite despite having a large variation in initial grain size of the starting aragonite (~2 to >100μm)[40]. Aragonite has a drastically different lattice configuration to that of dolomite and therefore cannot serve as a template for dolomite growth. Furthermore, as the unit cell volume of aragonite is significantly smaller than that of dolomite, the new formed dolomite must detach from the aragonite precursor during reaction because of lattice expansion. This detachment due to lattice expansion can explain the homogenous and fine-grained texture of dolomite produced from the aragonite seeds. Dolomite formation in this study followed the typically observed behaviour in laboratory dolomitization experiments of beginning as fine-grained, disordered (or poorly ordered) non-ideal dolomite which with time underwent dissolution and recrystallization to coarser-grained and better ordered dolomite. Experiments that were run at 130°C were incomplete containing mixtures of dolomite and other minerals, highlighting how difficult it can be to achieve complete dolomitization at much lower Earth-surface temperatures.

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