The "Dolomite Problem" Solved by the Flood

Michael J. Oard

Abstract

Dolomite conservatively makes up 10% of all sedimentary rocks and is mostly stoichiometric and ordered, mainly older than the Cenozoic. It can be thick and widespread, especially in the Precambrian and Paleozoic. Although dolomite is forming today, the great mystery is that it is of small scale and not stoichiometric and ordered. Dolomite today is likely formed by the aid of microorganisms that act as catalysts to overcome strong kinetic effects. The "dolomite problem" has been a uniformitarian mystery for over 200 years. Many uniformitarian scientists predominantly believe in replacement of limestone and not the primary precipitation of dolomite. However, replacement, or dolomitization, required tremendous fluid flow from a 'pumping mechanism' with an unlimited amount of Mg available. Evidence does exist for replacement, mainly from hydrothermal fluids associated with faults, but the fluid has to have been very hot. Numerous experiments studying the origin of dolomite use temperatures over 100°C for primary precipitation. In contrast, the short time scale of the Flood would require that most dolomite is primary formed from widespread hot water, especially very early in the Flood when the Precambrian and Paleozoic rocks were being deposited, mostly in basins and rifts. In addition, dolomites may be helpful as a criterion for determining the pre-Flood/Flood boundary.

Key Words: Carbonate, dolomite, dolomitization, dolostone, hydrothermal flow, Genesis Flood, geological column, limestone, Mg, microbial precipitation, pre-Flood/Flood boundary, protodolomite, replacement, uniformitarianism (actualism)

Introduction

The origin of several types of sedimentary rocks have remained major uniformitarian mysteries for a few hundred years. Dott (2003, p. 387) writes:

> When I was a student half a century ago, the origin of pure quartz sheet sandstones, then called orthoquartzites [now called quartz arenites], was considered a major puzzle. Together with the origin of dolomite, red beds, black shale, and banded iron formation, they made up a group of seemingly intractable geological problems. Even now, 50 odd years later, their origins are still being debated.

Dolomite is one of those mystery rocks (Figure 1). It was probably first discovered by the French geologist Deodat Guy de Dolomieu in 1792 in the Dolomite Mountains of northern Italy (Figure 2). Dolomite is the common name

Accepted for publication December 13, 2021

for carbonate rock mostly composed of the mineral dolomite ($CaMg(CO_3)_2$) (Boggs, 2012). It is sometimes called dolostone. To qualify as dolostone, more than 50% of the carbonate must be the mineral dolomite. Intermediates between limestone, calcite ($CaCO_3$), and dolostone are high-magnesium calcite or 'protodolomite' that is commonly synthesized in the lab.

Figure 1. Dolomite crystals from Trimouns Talc Mine, Luzenac, Ariège, Midi-Pyrénées, France (size 10 x 6.2cm) (Didier Descouens, Wikimedia Commons CC-BY-SA-4.0).

Sedimentary Rock Dolomite Mostly Stoichiometric and Ordered

Sedimentary rocks usually have a high percentage of either limestone or dolomite, but rarely possess much of the intermediates (Pettijohn, 1975). A perfectly stoichiometric, ordered dolomite with 50% calcium and 50% magnesium

Figure 2. Cristallo Mountain in the Dolomite Mountains of the southeast Alps in northeast Italy (Kallerna, Wikimedia Commons CC-BY-SA-4.0).

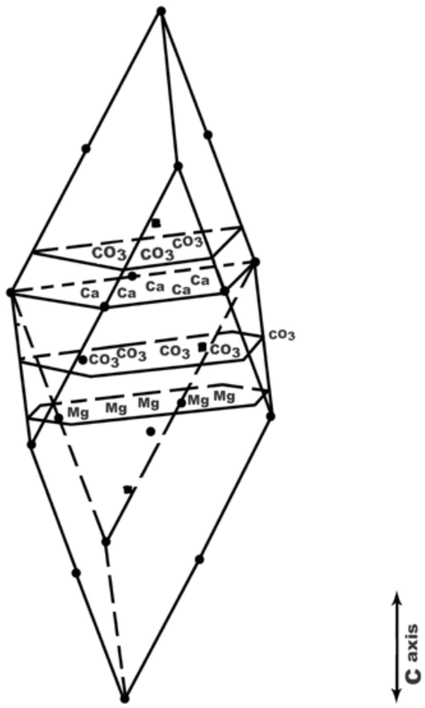

Figure 3. Ordered dolomite crystal (from Morrow, 1982, p. 8; redrawn by Mrs. Melanie Richard).

is rare. There is usually a small percentage more of calcium. The carbonate can have up to 14 mole % more Ca than Mg and still be called a dolomite (Manche and Kaczmarek, 2021). Most dolomites in sedimentary rocks are considered stoichiometric, especially in the Precambrian and Paleozoic, and ordered (Sperber et al., 1984; Manche and Kaczmarek, 2021). Ordered dolomite is the condition in which all calcium ions and all magnesium ions alternate in layers with the CO_3 ion in between (Figure 3). There is little or no mixture of calcium and magnesium ions in any one layer of the dolomite crystal. Dolomite can contain a small percentage of other elements, such as iron.

Many Dolomites Thick and Widespread

Although estimates vary, carbonate rocks make up from 20 to 25% of all sedimentary rocks (Boggs, 2012). Dolomite is more extensive than limestone in the Precambrian (Tucker, 1982). It is also poorly fossiliferous. The abundance of dolomite in the Proterozoic suggests that these rocks were deposited in a different environment from today: "The extraordinary abundance of dolomite in the Proterozoic challenges our understanding of Precambrian marine environments" (Hood et al., 2011, p. 871).

The amount of dolomite varies vertically through the Phanerozoic rock record, once claimed to be more than 50% of all carbonates in the Ordovician to Lower Carboniferous and the Triassic to Mid-Cretaceous of the geological column (Given and Wilkinson, 1987). Limestone dominates the late Paleozoic, the late Mesozoic, and the Cenozoic (Given and Wilkinson, 1987). However, many scientists dispute this trend, claiming the amount of dolomite increases with older age (Zenger, 1989; Manche and Kaczmarek, 2021). Petrash et al. (2017, pp. 559–560) write: "Independent of their origin, the distribution of dolostone in the rock record reflects an apparent monotonic decrease in abundance relative to limestone since the Palaeozoic…."

A conservative estimate of the amount of dolomite is that half the carbonate rocks are dolomite. And if carbonate rocks make up only 20% of all sedimentary rocks, then dolomite would make up about 10% of all sedimentary rocks—no small mystery to account for the origin of dolomite.

Dolomite can be thick and widespread through all the geological column. Fang and Xu (2018, p. 679) state: "Dolomite is one of the most common minerals in sedimentary rocks, ranging from Archean to Holocene." A massive Cambrian dolomite in the Yangtze Gorges area (China) "has a thickness ranging from several hundreds to more than one thousand meters across an area of ~500,000 square kilometers" (Ning et al., 2020, p. 2). The dolomite in the Dolomite Mountains of northern Italy is about 1,000 m thick (McKenzie and Vasconcelos, 2009). Petrash et al. (2017, p. 558) state: "Over the past century a number of models have been developed to explain the vast stratigraphic distribution of authigenic dolomite." Authigenic minerals are minerals formed in place within the sediments and were not transported into the sediments. Uniformitarian scientists consider even large dolomite formations to be authigenic because they believe they originated from a precursor limestone due to replacement (see below). Boggs (2009, p. 401) states that most dolomites are thick and widespread: "Let's return to the problem of explaining the relatively thick, massive, widespread dolomites that constitute most of dolomite in the geological record."

Stoichiometric, Ordered Dolomite Not Forming Today

Secular scientists, being strict uniformitarians, believe that by examining present processes, they should be able to solve the dolomite problem:

> We believe a major insight into the sedimentary dolomite problem can be obtained through detailed study of those environments where the mineral is forming at the present day under earth surface conditions. (Wacey et al., 2007, p. 156)

Dolomite has been discovered in small, warm, saline water since the 1950s, but it is not the volume or type found in the rock record. Dolomite has been discovered at many locations, including a hypersaline lagoon in Kuwait (Gunatilake et al., 1984); saline lakes in western Victoria, Australia (De Decker and Last, 1984); shallow ephemeral lakes in the Coorong region, South Australia (Rosen et al., 1989; Wacey et al., 2007); and in Dohat Faishakh Sabkha, Qatar (Shalev et al., 2021). Not only that, the dolomite is mostly protodolomite, not stoichiometric and not ordered. Other minerals are also precipitated, such as other carbonates and evaporites (Meister et al., 2013). This has been dubbed the "dolomite problem" (Manche and Kaczmarek, 2021).

Very Strong Kinetic Factors Inhibit the Formation of Dolomite Today

Presently seawater is 10–100 times supersaturated with magnesium (Warren, 2000), yet dolomite is not precipitating today. Land (1998) discovered that dolomite would not precipitate even at 1,000-fold supersaturation at temperatures of 25°C after 32 years. Very strong kinetic barriers have to be overcome. The main kinetic barrier is that Mg ions are surrounded by six water molecules, and it takes much energy to dehydrate the Mg ion so that it can bond: "Dehydration of water from surface Mg^{2+} is most likely the rate-limiting step in the dolomite growth at low temperatures" (Shen et al., 2015, p. 435). The energy barrier is 9.0–10.5 kcal/mole (Shen et al., 2015). Other kinetic inhibitors are the low concentration of dissolved CO_3^{2-} relative to Ca and Mg, the difficulty of ordering, and possibly high dissolved sulfate (Morrow, 1982; Petrash et al., 2017).

Microbes Likely Overcome the Kinetic Barriers Today

So why is dolomite locally forming at all today? It is likely because microorganisms act like catalysts and overcome the kinetic barriers for most precipitation of dolomite (Petrash et al., 2017). It is believed that extracellular polymeric substances excreted by anaerobic microbes cause the catalytic effect (Zhang et al., 2015). Researchers believe that the dolomite produced in the Kuwait lagoon was due to microbial sulfate reduction within the sediments (Gunatilake et al., 1984). The dolomite in Victoria and South Australia is believed to be primary but likely caused by bacteria (De Decker and Last, 1988; Wacey et al., 2007). This has given rise to the microbial theory for dolomite in the sedimentary rocks (McKenzie and Vasconcelos, 2009), but this theory is still under debate (Zhang et al., 2015). For instance, researchers have attempted to apply the microbial model to Ordovician dolomite/limestone laminations from the Appalachian Mountains in Pennsylvania (Fang and Xu, 2018). From the point of view of Flood geology, the microbial theory would be very unlikely, since there would not be enough time for microbes to act to deposit huge volumes of dolomite.

Origin of Dolomite Against Uniformitarianism

Therefore, the origin of dolomite is against uniformitarianism or actualism, the basis upon which almost all geology is interpreted. Hardie (1987, p. 176) states:

> This may explain the strong bias of modern dolomite to form in evaporitic environments, a bias not shared by ancient dolomites (with dolomites, the present is probably not the key to the past).

Ning et al. (2020, p. 1) claim:

> The origin of ancient massive dolostones, i.e. continuous dolostone sequence with a thickness >100 m and a platform-wide distribution, is the key issue of the 'Dolomite Problem' that cannot be clearly demonstrated by any existing dolomitization model individually or sequentially.

Scientists Believe Vast Majority of Dolomite Formed by Replacement

Although scientists think they can solve the dolomite problem by applying uniformitarianism, it is actually because they believe in uniformitarianism that they have a dolomite problem. By applying present processes, they believe dolomite forms at near present-day surface temperatures. Since massive dolomite is not forming today, and presumably in the past with near-present surface temperatures, the majority of geologists have come to believe in the replacement of limestone—for practically all dolomites, whether thick and widespread or local. Primary dolomite is dolomite that precipitates directly from solution, while replacement dolomite, also called dolomitization, is believed to have replaced limestone by high magnesium fluid flow. Tucker (1982, p. 11) states: "The majority of geologists accept that nearly all recent and ancient dolomites are of replacement origin and that primary dolomite is insignificant in the geological record." Kaczmarek and Sibley (2007, p. 424) write:

> Dolomite, $CaMg(CO_3)_2$, is a common mineral in ancient rocks and the thermodynamically stable carbonate phase in modern seawater, yet it is rare in modern marine environments. Why this is so has remained the subject of scientific inquiry of over 200 years. There is very little agreement concerning the details of dolomite formation except that most natural dolomites form at Earth-surface temperatures and pressures (Krauskopf and Bird, 1995). Despite such consensus it has been extremely difficult to synthesize dolomite abiotically at temperatures below 100°C [212°F], even over many years. (Land 1980, 1998)

If widespread, thick dolomite is to be formed by replacement, several conditions must be met. Tremendous fluid flow (Warren, 2000) with a 'pumping mechanism' and enough available Mg must occur. Not only that, the fluid flow must flush out the extra Ca liberated during dolomitization (Boggs, 2009). Furthermore, the porosity and permeability must allow the fluid flow.

The amount of available magnesium would have to be huge (Jones and Rostron, 2000), and the pump and fluid flow must continue for an extended period of time, since it is estimated that 1,000 units of fluid flow are needed to dolomitize one unit volume (Given and Wilkinson, 1987), and 350 kg of Mg is needed to dolomitize 1 m^3 of limestone with a porosity of 7% (Jones and Rostron, 2000). Of course the fluid flow of magnesium ions decreases away from a potential source—one of the many problems with dolomitizing a huge limestone formation. Such dolomitization needs to occur in the subsurface where temperatures are higher, but porosity and permeability is often reduced by compaction with depth. This is one reason why it supposedly would take millions of years for dolomite to form, according to uniformitarian reckoning. How reasonable is such a replacement process, even given millions of years?

Evidence for Replacement

There is evidence that replacement formed some dolomites. For instance, a close analysis of a 1,600 m-thick carbonate in eastern Spain showed massive dolomite near faults (Yao et al., 2020). It is assumed that hot Mg-rich water issued from the faults to dolomitize the limestone. Further evidence is provided by observations that certain beds are selectively dolomitized, limestone stringers exist within dolostones, and the dolostone ends abruptly. Another indication of replacement is that limestone fossils have been dolomitized, "Dolomitized fossils, ooids, peloids, reefs, and so forth all attest to dolomite replacement of original calcite or aragonite" (Tucker, 1982, p. 7). An ooid is a limestone coating on a small grain or fossil that is usually less than 1 mm in diameter, and they can grow rapidly in the Flood (Oard, 2021a). A peloid is generally another name for a large ooid. Reefs are a matter of interpretation and are likely carbonate banks with fossils.

Such fault-transported dolotomizing fluids were hot. Based on fluid inclusions in the affected rock, the temperature of dolomitization for a Cambrian dolomite in the Western Canadian Sedimentary Basin was 124°–181°C (Koeshidayatullah et al., 2020). It is believed that hot hydrothermal flow in a Triassic carbonate in southern Spain occurred at temperatures of 50–430°C (Mueller et al., 2020). From experimental dolomitization studies, Kaczmarek and Thornton (2017) discovered that cation ordering does not occur below 160°C despite reaction times as great as1,400 hours. Stoichiometry was also correlated with cation ordering.

Researchers sometimes use geochemical indicators, such as oxygen isotope ratios, to arrive at the temperature of dolomitization, but geochemical proxies give equivocal interpretations because of many variables that determine the oxygen isotope ratio. Tucker (1982, p. 10) states: "Many factors affect the fractionation of carbon and oxygen isotopes and determine the isotopic ratios of precipitated minerals." Ryan et al. (2020, pp. 2917–2918) state:

> Geochemical proxy data commonly permit multiple interpretation as to the temperature and chemistry of the dolomitizing fluids and environmental conditions (Machel, 2004), but frequently point to low-temperature near-surface settings…

Davies and Smith (2006, pp. 1655–1656) write that oxygen isotopes understate temperatures for dolomitizing fluid:

> An important corollary of this relationship is that, if the temperature of the fluid forming the dolomite is estimated from $\delta^{18}O$ data assuming a seawater or slightly modified seawater composition (for example, Green and Mountjoy, 2005), an erroneously low fluid temperature may be determined if the precipitating water was a hypersaline brine. This error may be very large…

Oxygen isotope ratios depend upon many variables, such as the oxygen isotope ratio of the fluid, of the carbonate that is replaced, and the temperature of precipitation (Lapponi et al., 2014).

Thus, many researchers believe in the hydrothermal model for dolomitization because of the very hot temperatures required for primary dolomite. Based on a dolomite from northern Spain, Lapponi et al. (2014) determined that hydrothermal dolomitization occurred at temperatures of 80–120°C. So, hot temperatures seem to be required for replacement of limestone:

> The degree of order and the stoichiometry of the dolomite product is a function of both the temperature and length of time of the reaction. Increase in temperature or greater length of time results in a more ordered and stoichiometric dolomite. (Gregg and Sibley, 1984, p. 914)

Temperatures >100°C Needed for Primary Precipitation

There have been numerous experiments forming dolomite in the lab at higher temperatures. It is known that dolomite much more easily precipitates at higher temperatures, higher Mg/Ca ratios, and high Mg supersaturation (Burns et al., 2000). Scientists used to think high sulfate inhibited the formation of dolomite (Wright, 1997), but this has likely been disproven (Zhang et al., 2012). Stoichiometry and ordering increase under these conditions, similar to many dolomites found in the rock record. Hot water is required for primary precipitation of dolomite: "Only at temperatures over about 100°C, well beyond those expected for synsedimentary dolomite formation, can dolomite be readily precipitated in experiments" (Burns et al., 2000, p. 53). Morrow (1982, p. 6) states:

> The absence of a widely accepted theory concerning the chemistry of dolomitization is due primarily to the difficulty in precipitating dolomite from appropriate solutions at temperatures less than 100°C.

Hardie (1987, p. 166) states: "At elevated temperatures the dolomite problem essentially disappears (ordered dolomite can be made in the laboratory in days at 100°C)." Machel and Mountjoy (1986, pp. 185, 190) state:

> …and to date it has not been possible to experimentally precipitate stoichiometric, well ordered dolomite below 100°C. … Beyond about 100°C this kind of diagram is rendered meaningless since almost all know kinetic inhibitors become ineffective.

The temperature should be over 150°C, and the higher the temperature, the faster dolomite precipitates and the more ordered the atomic structure (Arvidson and MacKenzie, 1999; Li et al., 2015). High temperatures are used to study the formation of dolomite in the lab, which should provide a hint to the conditions needed to form dolomite rapidly, such as in the Flood (see below): "High temperature experiments (>100°C) provide insight into the general process of dolomitization…" (Nordeng and Sibley, 1994, p. 191).

The Claim that Many Precambrian Dolomites are Primary

Not only is there more dolomite in the Precambrian than the Phanerozoic by volume percent, but some scientists believe Precambrian dolomites are primary. In fact, early geologists first assumed the dolomite was primary (Glover and Sippel, 1967). Based especially on the Beck Springs Dolomite in the Death Valley region of the United States and the Porsanger Dolomite in Arctic Norway, Tucker (1982, p. 7) states:

> The data suggest that in Precambrian time dolomite was the principal carbonate mineral precipitated from seawater and during diagenesis, and this implies that Precambrian seawater was different from that of the Phanerozoic.

One of Tucker's main evidences is that the replacement destroys the limestone fabric, but this has been questioned (Ricketts, 1982; Zenger, 1982).

Dolomite Shows Early Floodwaters Were Very Hot

It is possible that some Precambrian dolomite is from the very early Flood (Oard and Reed, 2017; Oard, 2021b). The large scale of some dolomites in the rock record matches the scale of sedimentation expected in the Flood. Because of the short time available for forming thick, widespread dolomites, many dolomites are likely primary. Replacement dolomites would be localized near faults, as in the Ordovician section in the Williston Basin, by hydrothermal flow of very hot water. Precipitation of dolomite requires water over 100°C. This would have been early in the Flood, when some Precambrian and all Paleozoic rocks were deposited. Since limestone was also precipitated, this primary dolomite formation likely occurred on a local to regional scale, and mainly in basins and rifts. The increasing proportion of limestone over time suggests increasingly cooler water, possibly because deposited sediments insulated the Floodwaters from deep, hot rocks. It is also possible that there was more mixing with cooler seawater.

Implications for Flood Models

Local, very hot early Floodwaters have several implications (Oard, 2021b). Dolomite may be a criterion for determining the pre-Flood/Flood boundary. There does not seem to be any significant change in dolomite/limestone ratios from the Precambrian up into the Paleozoic, suggesting that these rocks are all Flood rocks. Moreover, the high percentage of dolomite in the Precambrian and the consistency through the late Paleozoic would indicate many dolomites were deposited in the Flood, not before. Since dolomite even occurs in the Archean, it could imply that some Flood rocks even extend into the Archean. Such a deduction is reinforced by raindrop imprints, black shale, and impacts in the Precambrian that continue up into the Paleozoic (Oard, 2013, 2014).

A Flood model must account for hot water early in the Flood. Very hot water could have resulted from several mechanisms such as the eruption of the "fountains of the great deep," volcanism, tectonic friction, and impacts. The early hot temperatures, especially in the developing Precambrian and Paleozoic basins and rifts, could account for the present-day geothermal gradient of 25–30°C/km (Fridleifsson et al., 2008) in sedimentary rocks of the subsurface. The subsurface was not necessarily heated by millions of years of accumulating overburden, as uniformitarian scientists believe, but by the deposition of sediments in hot water early in the Flood. Such hot water temperatures, plus overburden, could also account for the rapid origin of coal and oil in the Flood.

Conclusions

Dolomite, a common rock, has been a uniformitarian mystery for over 200 years. It is uniformitarianism that creates the "dolomite problem." Dolomite cannot be deposited under normal surface temperatures because of very strong kinetic barriers. However, dolomite is being precipitated locally today, likely because microbes catalyze the kinetic factors. But this dolomite is not stoichiometric or ordered like practically all sedimentary dolomite. Experiments have shown that very hot temperatures also overcome the kinetic barriers for primary precipitation. But uniformitarianism would have us believe that mean water temperatures were never very hot. Therefore, they believe dolomite forms by replacement of limestone, but this also requires hydrothermal flow through faults. It is also highly unlikely that replacement dolomitization can account for all of the thick, widespread layers documented throughout the world.

The short timescale of the Flood requires formation of primary dolomite. This implies that very early Floodwaters were very hot locally and probably were present in rifts and basins. Since there is no significant change in the percentage of dolomite, as well as other geological variables, through at least the early Paleozoic, it is unlikely that late Neoproterozoic and Precambrian/Cambrian boundaries mark a universal pre-Flood/Flood boundary.

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