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Letter

The Dolomite Problem: A Matter of Time

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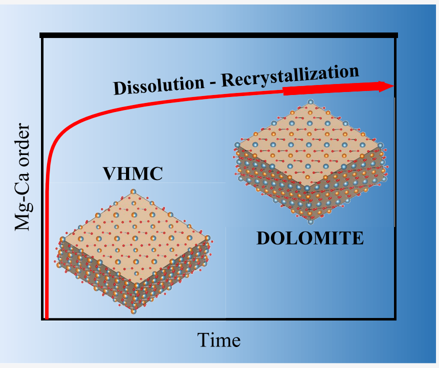
ABSTRACT: Why is the mineral dolomite, $CaMg(CO_3)_2$, abundant in ancient sedimentary rocks but scarce in modern rock-forming environments? What are the natural processes that lead to the characteristic Mg−Ca order in the dolomite structure? These important geological questions have captivated the interest of geoscientists for over a century, but the answers still remain elusive. Only recently, by the development of experimental work and the generation of large geochemical data sets, we began to suspect that both the formation and Mg−Ca ordering of dolomite could be the result of progressive dissolution−(re)crystallization reactions extended over large geological periods of time. Here, we present an initial estimate of dolomite cation-ordering times derived from previously reported data of Phanerozoic dolomites. This result provides new insight into the process of dolomite formation in nature, and it clearly suggests that can be possible to precisely determine the kinetics of the Mg−Ca ordering of natural dolomites.



KEYWORDS: *dolomite, $CaMg(CO_3)_2$, Mg−Ca order, carbonate mineral, sedimentary rock*

Dolomite, $CaMg(CO_3)_2$, is an abundant carbonate mineral in ancient rock formations, but it is extremely scarce in modern sedimentary environments. This intriguing observation has been repeatedly referred to as the "dolomite problem" in the geological literature.[1−5] Many geoscientists over time have almost obsessively searched for a solution to this enigma without being able to come up with a clear answer.[6] This makes us wonder whether the right question to answer is why dolomite does not easily form at present but rather how long does it take to form highly ordered dolomite in a carbonate-depositing geological environment.

A vast number of experimental works and calculations indicate that dolomite formation can occur in several stages of replacement and recrystallization.[7−19] In recent decades, some field and geochemical studies have also shown that the sedimentary and diagenetic formation of dolomite can be extended over thousands to millions of years.[20−22] Therefore, it is currently agreed that, after a relatively rapid initial dolomitization process, a subsequent increase in the Mg−Ca order in the dolomite crystals can occur via secondary recrystallization operating over geological periods of time.[23−25] This makes some researchers think that the systematic measurement of cation ordering of dolomites over time can provide relevant information on the kinetics of dolomite formation in nature.

In the last 2 years, Pina et al.[5] and Manche and Kaczmarek[26] reported large data sets consisting of cation-ordering values (i.e., $I_{01.5}/I_{11.0}$ intensity ratios measured on diffractograms) of sedimentary dolomites from various geological ages through the Phanerozoic (Figure 1).

As Figure 1 shows, dolomites older than about 30−40 million years have maximum $I_{01.5}/I_{11.0}$ values. In turn, the cation order of dolomites formed more recently shows a sharp increase over time. This strongly suggests that dolomite cation ordering occurs by progressive recrystallization taking place long after sedimentation.[5,26] In such a case, the quantification of dolomite-ordering kinetics from recorded data would be possible. However, this first requires proposing a plausible empirical rate equation. Kell-Duivestein et al.[27] recently reported the use of the following equation to determine the increase in cation order over time for dolomites synthesized in the laboratory at different temperatures:

$$y = k \ln(t) + c \qquad (1)$$

where y is the dolomite order index, $I_{01.5}/I_{11.0}$, k is a kinetic coefficient for cation ordering, t is the reaction time, and c is the dolomite order index when $t = 0$. The use of this first-order reaction kinetic approach allowed Kell-Duivestein et al.[27] to adequately describe the evolution of the cation order of dolomites during approximately 1 year of ripening in an aqueous medium at various temperatures. Furthermore, from eq 1, Kell-Duivestein et al.[27] extrapolated cation-ordering rates, concluding that, at 25 and 50 °C temperatures, highly ordered

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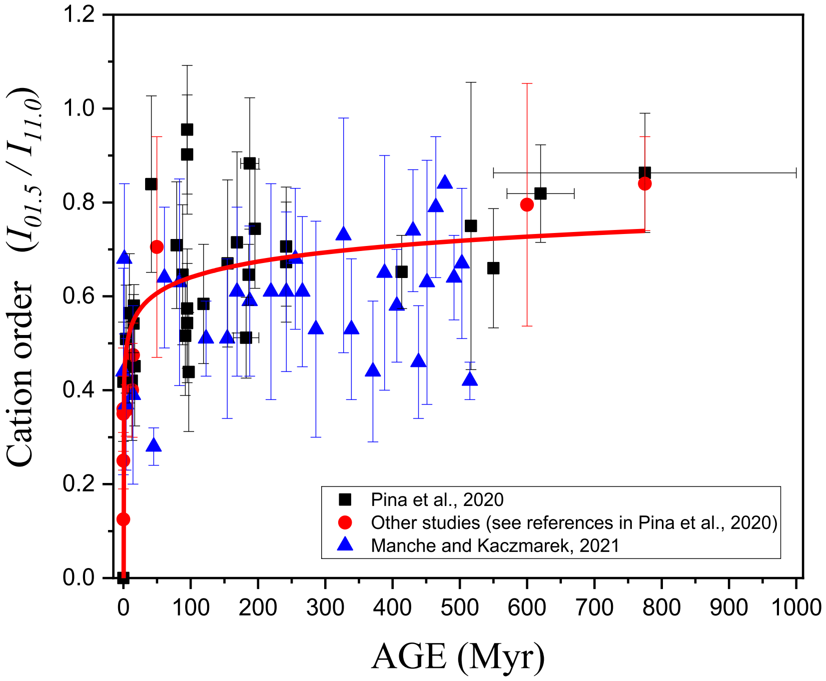

Figure 1. Cation order ($I_{01.5}/I_{11.0}$ intensity ratios) versus dolomite age in million years through the Phanerozoic and late Proterozoic. The red line [$y = 0.048 \pm 0.012 \ln(x) + 0.418 \pm 0.051$] has been fitted to all data points using the orthogonal distance regression method (regression coefficient $R^2 = 0.999$). See the explanation in the main text.

dolomite will only form after an ordering process extending over 6.8 and 1.4 million years, respectively. This is an important outcome, because it provides first estimates of times of dolomite cation ordering in sedimentary environments from experimental data.

Interestingly, eq 1 can also be used to describe the increase in the $I_{01.5}/I_{11.0}$ order index over time in natural dolomites, as shown in Figure 1. When this equation is fitted to the reported $I_{01.5}/I_{11.0}$ values for dolomites formed in the last 775 million years (see the red line in Figure 1), we obtained the following empirical equation:

$$\text{cation order} = 0.048\ (\pm 0.012)\ \ln(\text{AGE}) + 0.418\ (\pm 0.051) \quad (R^2 = 0.999) \tag{2}$$

Although eq 2 has been fitted to a relatively scattered data set and must, therefore, be approached with caution, some general conclusions can be drawn. First, the good fit of the equation proposed by Kell-Duivestein et al.[27] to the $I_{01.5}/I_{11.0}$ values and the ages of natural dolomites (eq 2) strongly suggests that the increase in cation order observed in both natural and synthetic dolomites essentially takes place by the same recrystallization mechanism.[24,25] Second, dolomites with a high cation order (i.e., with $I_{01.5}/I_{11.0} > 0.6$) are usually older than 40 million years (see Table 1). Third, eq 2 reveals that Mg−Ca cation ordering is a relatively rapid process during the first million years after sedimentation, which then slows to reach maximum $I_{01.5}/I_{11.0}$ values.

Table 1. Estimated Times To Reach $I_{01.5}/I_{11.0}$ Values Ranging from 0.1 (Dolomites, Poorly Ordered) to 0.7 (Dolomites, Highly Ordered) Calculated Using Eq 2

cation order ($I_{01.5}/I_{11.0}$)	time (million years)
0.1	0.001
0.2	0.011
0.3	0.088
0.4	0.696
0.5	5.493
0.6	43.364
0.7	342.319

The ordering times listed in Table 1 show that the formation of sedimentary dolomites with typical degrees of cation order (i.e., $I_{01.5}/I_{11.0}$ higher than 0.5) requires an ordering process operating over a million years. This closely follows the geological time scale for dolomite cation ordering extrapolated from the experimental data by Kell-Duivestein et al.[27] However, dolomite ordering times estimated by Kell-Duivestein et al.[27] seem to be significantly shorter than those calculated using eq 2 and the data plotted in Figure 1. Such a discrepancy can be partly due to the unavoidable uncertainty derived from extrapolating an equation fitted to data collected over a year[27] to very long geological times (i.e., millions of years). Furthermore, there is an array of factors that can affect the ordering kinetics and the maximum degree of order that natural dolomites can reach. Thus, while deviations from the ideal dolomite stoichiometry of Mg/Ca = 1 and the presence of impurities (e.g., Fe and Mn) reduce maximum cation order values,[28] the kinetics of dissolution−(re)crystallization reactions strongly depend upon the characteristics of interstitial fluids and the consistency of sediments and rocks.[3,4,27,29] In this regard, experimental work has shown that the temperature and chemical composition of dolomitizing fluids (Mg/Ca ratios, sulfate concentration, saturation states, salinity, alkalinity, etc.) can considerably affect the kinetics of the different processes that lead to the formation of dolomite.[25,30−33] Consequently, local variations in the composition of subsurface fluids can result in deviations from the cation-ordering kinetics expressed by eq 2. These deviations from the general trend shown in Figure 1 are relatively frequent, and they may be useful to identify particular conditions for dolomite formation, i.e., conditions that favors or retard the Mg−Ca ordering of dolomites. Therefore, future studies should undoubtedly consider in detail internal (i.e., crystallochemical) and external (geological environment) factors to accurately determine the time evolution of cation ordering in natural dolomites. Nevertheless, the current state of knowledge indicates that resolving the long-vexing dolomite problem is just a matter of time.

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Notes

The authors declare no competing financial interest.

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