Dissolution-precipitation reactions controlling fast formation of dolomite under hydrothermal conditions

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ARTICLE INFO

ABSTRACT

In laboratory experiments, the precipitation of dolomite at ambient temperature is virtually impossible due to strong solvation shells of magnesium ions in aqueous media and probably also due to the existence of a more intrinsic crystallization barrier that prevents the formation of long-range ordered crystallographic structures at ambient surface conditions. Conversely, dolomite can easily form at high temperature (>100 °C), but its precipitation and growth requires several days or weeks depending on experimental conditions. In the present study, experiments were performed to assess how a single heat-ageing step promotes the formation of dolomite under high-carbonate alkaline conditions via dissolution-precipitation reactions. This reaction pathway is relevant for the so-called hydrothermal dolomite frequently observed in carbonate platforms, but still ill-defined and understood. Our precipitation route is summarized by two main sequential reactions: (1) precipitation of Mg-calcite at low temperature (~20 °C) by aqueous carbonation of synthetic portlandite ($Ca(OH)_2$) in a highly alkaline medium (1 M of NaOH and 1 M of $MgCl_2$), leading to precipitation of oriented nanoparticles of low- and high-Mg calcite (~79 wt%) coexisting with aragonite (~18 wt%) and brucite (~3 wt%) after 24 h; (2) fast dolomitization process starting from 1 h of reaction by a single heat-ageing step from ~20 to 200, 250 and 300 °C. Here, the Mg-calcite acts as a precursor that lowers the overall kinetics barrier for dolomite formation. Moreover, it is an important component in some bio-minerals (e.g. corals and seashells). Quantitative Rietveld refinements of XRD patterns, FESEM observations and FTIR measurements on the sequentially collected samples suggest fast dolomite precipitation coupled with dissolution of transient mineral phases such as low-Mg calcite (Mg < 4 mol%), high-Mg calcite (Mg > 4 mol%), proto-dolomite (or disordered dolomite; Mg > 40 mol%) and Ca-magnesite. In this case, the dolomite formation rate and the time-dependent mineral composition strongly depend on reaction temperature. For example, high-purity dolomitic material (87 wt% of dolomite mixed with 13 wt% of magnesite) was obtained at 300 °C after 48 h of reaction. Conversely, a lower proportion of dolomite (37 wt%), mixed with proto-dolomite (43 wt%), Ca-magnesite (16 wt%) and high-Mg calcite (4 wt%), was obtained at 200 °C after 72 h. The present experiments provide an additional mechanism for the massive dolomite formation in sedimentary environments (ex. deep sea organic-rich carbonate-sediments) if such sediments are subjected to significant temperature variations, for example by hot fluid circulations related to volcanic activity. In such systems, organic degradation increases the carbonate alkalinity (HCO_3^-) necessary to induce the dolomitization process at low and high temperature.

1. Introduction

The formation and structural properties of dolomite ($CaMg(CO_3)_2$) have been investigated in the past two centuries because this mineral can be found throughout the Earth's crust and is associated with several elements of economic importance (including the so-called rare earth elements) and hydrocarbon deposits (e.g. McKenzie, 1991; Warren, 2000; Davies and Smith, 2006; Sanchez-Roman et al., 2009; Mckenzie and Vasconcelos, 2009; Deelman, 2011; Xu et al., 2013). However, various questions still remain debated concerning the formation mechanisms and kinetics of dolomite in natural systems as well as its synthesis in the laboratory. Moreover, the scanty distribution of recent dolomite in

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natural environments contrasts strongly with its abundance in ancient sedimentary rocks of marine origin, leading to the paradox commonly referred to as the "dolomite problem" (Compton, 1988; Arvidson and Mackenzie, 1997, 1999). Dolomite is a complex mineral because it can precipitate either via a diagenetic mineral replacement mechanism or through hydrothermal and/or metamorphic mechanisms. For all these mechanisms, fluid flow and sufficient magnesium in the interacting fluid are required. This complexity has been debated in recent decades and has led to various interpretations on the origin of dolomite in geological formations (Warren, 2000; Mckenzie and Vasconcelos, 2009; Jacquemyn et al., 2014).

It has been observed that dolomite can form in lakes, on or beneath shallow seafloors, in zones of brine reflux and in early to late burial settings (Warren, 2000). More recently, various studies have proposed that bacterial metabolism may aid the process of dolomite nucleation and precipitation in shallow environments such as hypersaline anoxic lakes where the presence of sulfate-reducing conditions and microbial activity are observed (e.g. Warren, 2000; Warthmann et al., 2000; Kenward et al., 2009; Deng et al., 2010). In addition, hot hydrothermal fluids may circulate in carbonate platforms during burial diagenesis. Fluid temperature may increase via volcanic activity (e.g. igneous intrusions, sill and dike emplacement), and hydrothermal systems could be created at a local and/or regional scale (e.g. Blendinger, 2004; Davies and Smith, 2006; Jacquemyn et al., 2014). In such cases, the replacement of limestone by dolomite could be significantly enhanced if sufficient amounts of magnesium are supplied to the system (Jacquemyn et al., 2014). Under such burial conditions, magnesium could originate from various sources, such as seawater, dissolution of ultrabasic rocks (when igneous intrusions and/or hydrothermalism are present), and dissolution of preexistent Mg-carbonates (e.g. low and high Mg-calcite, magnesite, brucite and proto-dolomite) contained in fossil organisms (e.g. seashells, corals and coralline algae) abundant in carbonate platforms. In these non-equilibrated systems, organic degradation can also lead to a significant increase in the carbonate alkalinity ($2CH_2O$ (organic matter) + $SO_4^{-2} \rightarrow H_2S + 2HCO_3^-$) of interacting fluids via bacterial and/or thermochemical sulfate reduction (e.g. Compton, 1988; Warren, 2000; Machel, 2001; Nash et al., 2011).

High carbonate alkalinity and temperature are crucial parameters to enhance the dolomitization processes in natural hydrothermal systems (Machel, 2001; Jacquemyn et al., 2014), as recently demonstrated in the laboratory (Montes-Hernandez et al., 2014). In this context, the so-called hydrothermal dolomite (HTD), as defined by Davies and Smith (2006), was observed in several carbonate formations, for example, in the Devonian and Mississippian of the Western Canada sedimentary basin, in the Ordovician of the Michigan and Appalachian basins of eastern Canada and northeastern United States, in the Cretaceous of onshore and offshore Spain, in the Anisian-Ladinian Latemar platform of northern Italy and many other locations (Davies and Smith, 2006; Jacquemyn et al., 2014 and references therein). In these studies, stable isotopes of oxygen (^{18}O) and carbon (^{13}C), fluid inclusion re-homogenization temperature and salinity and petrographic/textural criteria were used to discriminate low-temperature dolomite from hydrothermal dolomite (>80 °C). The presence of superstructure-ordering reflections in X-ray diffraction spectra, as previously defined by Lippmann (1973), is the main characteristic of hydrothermal dolomite. However, this simple crystallographic criterion is rarely used. Accordingly, at low temperature only disordered dolomite (or proto-dolomite) can be formed, as discussed below. In the present study, several laboratory experiments were performed to assess how a single heat-ageing step promotes the formation of ordered dolomite (i.e. with superstructure-

ordering reflection in XRD patterns) under high-carbonate alkaline conditions via dissolution-precipitation reactions.

Experimental physicochemical conditions, reaction mechanisms and kinetics at which dolomite can be formed provide new insights for a better understanding of dolomite formation. Several studies have demonstrated that the formation of dolomite at ambient temperature is virtually impossible or that geological time scales are probably required (Deelman, 2001; Pimentel and Pina, 2014). This limitation has been related to the strong salvation shells of magnesium ions in aqueous media; a similar situation exists for magnesite ($MgCO_3$) which raises the same difficulty of precipitating at room temperature and atmospheric pressure in laboratory experiments (Deelman, 2001, 2011; Xu et al., 2013). A recent study reported on the synthesis of $MgCO_3$ and $Mg_xCa_{1-x}CO_3$ (0 < x < 1) solid phases at ambient conditions in the absence of water, i.e. using formamide as solvent (Xu et al., 2013). This study suggests the existence of a more intrinsic crystallization barrier that prevents the formation of long-range ordered crystallographic structures ($R\overline{3}2/c$ in magnesite and $R\overline{3}$ in dolomite) at ambient conditions.

On one hand, various authors have claimed that dolomite formation at ambient laboratory conditions is possible by using bio-assisted systems. In such studies, sulfate-reducing or aerobic heterotrophic bacteria, hypersaline or seawater solutions and anoxic or oxic conditions have been used (e.g. Warthmann et al., 2000; Sanchez-Roman et al., 2009; Kenward et al., 2009; Deng et al., 2010; Krause et al., 2012). However, the reported X-ray diffraction patterns do not clearly show the presence of the superstructures characteristic of dolomite (ordering reflections at 22.02 (101), 35.32 (015), 43.80 (021), etc. 2θ, see Lippmann (1973)). These superstructure reflections are related to the alternating regular monolayers of Ca and Mg perpendicular to the c-axis of ordered dolomite crystals.

On the other hand, ordered dolomite can be synthesized at higher temperatures (>100 °C) by mixing (fast or slowly) two pre-defined solutions, one containing Mg/Ca (ratio ≥1) and the other containing dissolved carbonate ions (Medlin, 1959; Arvidson and Mackenzie, 1999; Deelman, 2001), or by placing high-purity calcite or limestone material in contact with Mg-rich solutions (Grover and Kubanek, 1983; Dockal, 1988; Kaczmarek and Sibley, 2011; Etschmann et al., 2014; Jonas et al., 2015). Both synthesis methods require several days or weeks depending on experimental conditions. Therefore, identifying novel and/or innovative abiotic or biotic synthesis methods for dolomitic materials under a broad spectrum of experimental conditions remains a major challenge in order to obtain a better understanding of its formation in natural systems.

In a previous study, it was demonstrated that ordered dolomite can be precipitated via simultaneous dissolution of calcite and magnesite under hydrothermal conditions between 100 and 200 °C (Montes-Hernandez et al., 2014). The high-carbonate alkalinity in the interacting solution significantly promoted the formation of dolomite with respect to pure water as initial interacting fluid. However, about 90 days were required to obtain 50% of ordered dolomite in the solid at 200 °C. Based on this previous study, new experimental conditions are explored here using semi-continuous dispersed reactors. In these experiments, high-magnesium calcite is first produced at ambient temperature, maintaining a constant carbonate alkalinity. The Mg-calcite produced acts as a precursor for the dolomitization process when a fast heating step occurs in the system, mimicking for example, volcanic activity or the circulation of hot (200−300 °C) fluids in the crust. Under these conditions, the precipitation of dolomite can be very fast. In addition, various aliquots of suspensions were withdrawn from the reactor as a function of time in order to obtain specific information on the kinetics and reaction mechanism. With