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Dolomite dissolution in aqueous solutions in the presence of nucleotides and their structural components at 25 °C and pCO_2 ~1 atm

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ABSTRACT

The kinetics and stoichiometry of dolomite dissolution were investigated in deionized water at 25 °C and pCO_2 ~1 atm in the absence (control) and presence of various nucleotides and their structural components at low concentrations (1 mM). Dissolutions were conducted in "free-drift" mode and rates estimated based on the accumulation rate of calcium and magnesium ions in solution. The additives considered in this study are likely present at low concentrations (< mM) in deep, carbonate aquifers targeted for CO_2 geological sequestration. Results of our control experiment are consistent with rates and stoichiometries reported in earlier studies. In the presence of nucleotides, dolomite dissolution was inhibited and proceeded incongruently, yielding a Mg:Ca solution ratio ≥ 2. An investigation of the nucleotide structural components (nucleosides, nitrogenous bases and phosphates) revealed that, whereas they nearly all inhibited dolomite dissolution, only phosphate salts (mono-, di-, tri-, and hexametaphosphate) lead to incongruent dissolution. Examination of the surface morphology and phosphate analysis of the solids reacted in the presence of nucleotides and phosphate salts revealed the formation of a solid phosphate phase on the dolomite surface, likely a Ca rich-phosphate phase that accounts for the observed dissolution incongruency.

1. Introduction

Carbonate reservoirs are hosts to > 50% of the world's hydrocarbon reserves (Saberi, 2010). The Western Canadian sedimentary basin (central Alberta and southwest Alberta and Manitoba) comprises a number of ancient carbonate reefs, many of which have been partially or fully dolomitized, and these account for a substantial percentage of oil (50.7%) and gas (23%) producing reservoirs in Canada(Creaney and Allan, 1990; Fowler et al., 2001; Halbertsma, 1994; Hamilton and Olson, 1990; Hay, 1994). In many cases, the porosity and permeability of these reservoirs was acquired as a result of dolomitization (Qing and Mountjoy, 1992; Sharma et al., 2014) and are now identified as potential sites for geological sequestration of CO_2 (Bachu, 2003; Bachu and Adams, 2003; Bachu and Stewart, 2002). The injection and dissolution of CO_2 in these reservoirs will lower the pH of the reservoir fluids and promote the dissolution of surrounding carbonate minerals (André et al., 2007; André et al., 2010; Garcia et al., 2011; Hao et al., 2013; Luquot and Gouze, 2009; Mohamed et al., 2011; Tutolo et al., 2014). The dissolution and precipitation of carbonate minerals in aqueous solutions at high CO_2 partial pressures is of growing research interest in the context of the geological sequestration of CO_2 in deep aquifers (Oelkers et al., 2011; Oelkers and Schott, 2005; Wellman et al., 2003).

Dolomite is a double carbonate, in which the cationic layer alternately hosts calcium and magnesium ions (Morse et al., 2007; Warren, 2000). Dolomite is abundant in ancient rocks, fossil carbonate reefs, but rare in modern sedimentary deposits (Arvidson and Mackenzie, 1999; McKenzie and Vasconcelos, 2009; Warren, 2000). A large number of studies have been carried out to determine the kinetics of dolomite dissolution in aqueous solutions in an effort to identify factors that control the reaction (Busenberg and Plummer, 1982; Pokrovsky and Schott, 2001; Sherman and Barak, 2000; Lüttge et al., 2003; Urosevic et al., 2012), more recently in the context of geological CO_2 sequestration and the structural integrity of limestone reservoirs (Gautelier et al., 2007; Luhmann et al., 2014; Pokrovsky et al., 2009a; Pokrovsky et al., 2005; Pokrovsky et al., 2009b), but also in an attempt to resolve the mysteries of its formation at low temperatures (Busenberg and Plummer, 1982; Chou et al., 1989; Gautelier et al., 1999; Herman, 1982; Herman and White, 1985; Morse and Arvidson, 2002; Morse et al., 2007; Orton and Unwin, 1993; Pokrovsky et al., 1999).

McKenzie and Vasconcelos (2009) recently reported that bacteria can promote the precipitation of dolomite. Bacteria and their metabolic

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products are ubiquitous in subaqueous environments (Dhami et al., 2013; Gray and Engel, 2013; Paul, 2014) and the former can thrive in carbonate (calcite and dolomite) hydrocarbon-bearing reservoirs (Machel et al., 1995; Wolicka et al., 2010). Hence, these reservoir rocks and associated fluids may contain bioactive molecules such as nucleotides (Bulleid, 1978; Holm Hansen and Booth, 1966; Karl and Craven, 1980; Oomori and Kitano, 1991; Webster et al., 1984) that may influence the dissolution and growth of carbonate minerals (calcite and dolomite) in these environments. Numerous studies have been conducted to determine the effects of temperature, pH, salinity and pCO_2 on the dissolution of Ca and Mg carbonates (Chou et al., 1989; Pokrovsky et al., 2005; Pokrovsky et al., 2009b; Zhang et al., 2007), but few have focused on the influence of organic ligands on the reaction (Jordan et al., 2007; Oelkers et al., 2011; Pokrovsky et al., 2009a). Meyer (1984) reported on the influence of several additives, including nucleotides (ATP and ADP), on calcite growth rates from aqueous solutions. His results show an inhibition of calcite growth upon an increase in additive concentration, but no study of the influence of nucleotides on carbonate dissolution kinetics has been conducted to date. The present study strives to partially fill this gap by reporting the results of an experimental study of the kinetics and stoichiometry of dolomite dissolution in the absence (control) and presence of four nucleotides (ATP, ADP, GDP and AMP) and their structural components (nucleosides, purines, sugars and phosphate backbone). Experiments were carried out in deionized water at a CO_2 partial pressure of one atmosphere in order to identify the chemical constituents responsible for the inhibitory and incongruent dissolution of the mineral that we observed in the presence of the nucleotides.

2. Materials and methods

2.1. Sample characteristics

Dolomite crystals (hydrothermal, from Franklin, Sussex County, NJ, U.S.A.), purchased from Boreal Science, were used in all experiments. The material was crushed, ground in an agate mortar and pestle, and sized by dry sieving between 149 and 212 μm. The sized material was washed 5 min in a 0.05 N hydrochloric acid (HCl) solution to remove fine particles and impurities, separated from the solution by filtration through a 0.45 μm Millipore polycarbonate filter, rinsed five times with deionized water, and allowed to dry at room temperature. The geometric surface area of the ground material was estimated at 155 cm^2/g based on the mean grain size (180.5 μm) and the correlation published by Plummer and Wigley (1976) for particles sized between 20 and 325 mesh. The mineralogy of the material was characterized by X-ray diffraction (XRD) (Rigaku Smartlab: Cu Kα anode at 44 mA, 2θ step size of 0.01 degree and scan speed of 1.5 deg/min) whereas its metal (Ca, Mg, Fe, Mn, Na and Sr) content (Table 1) was determined by Flame Atomic Absorption/Emission Spectrometry (AAS) (Perkin Elmer Analyst 100 Atomic Absorption Spectrometer) following dissolution of a known weight of the material in 5 N HCl and further dilution in 0.1 N HCl. The AAS was calibrated using external standards prepared by dilution, in 0.1 N HCl, of commercially purchased 1000 ppm certified solutions. The results of the AAS and XRD analyses revealed that the sample is a calcium-rich dolomite having 56.7% $CaCO_3$ and 43.3% $MgCO_3$ (CaO-31.8% and MgO-20.9%) with < 5% $FeCO_3$. The excess calcium in the dolomite can be explained by the presence of a ferroan dolomite (ankerite) that we identified by XRD Rietveld analysis (Chai et al., 1995).

Table 1
Metal composition of the dolomite.

Element	Concentration (ppm)
Calcium (Ca)	20,600
Magnesium (Mg)	9260
Iron (Fe)	830
Manganese (Mn)	175
Sodium (Na)	9.2
Strontium (Sr)	53

2.2. General procedure

The dolomite dissolution rate measurements were carried out in “free-drift” mode at 25 °C, 1 atm CO_2 partial pressure in a 500 mL jacketed reaction vessel. The experimental set-up is schematically represented in Fig. 1. Temperature was maintained constant by recirculating water through the jacketed vessel from a water bath set at 25.0 ± 0.1 °C. The reaction vessel was fitted with a PVC lid with holes for insertion of a Teflon stirring impeller, CO_2 gas dispersion tube and pH combination electrode. The impeller was driven by an overhead motor at a stirring speed of 120 rpm, high enough to keep the solid particles in suspension.

The dissolution experiments were carried out in 300 mL of deionized water in the absence (control experiment) and presence of selected additives (Table 2) at an initial concentration of 1 mM. The additives were chosen because of their potential presence in natural sedimentary environments and their ability to complex divalent cations. The initial pH of the solution was adjusted between 4 and 5 using standardized HCl (0.1 M) or NaOH (1 M) solutions. Commercial grade CO_2 (100%) was pre-saturated with water by bubbling the gas through a scrubber filled with deionized water before being channeled into the reaction vessel through a fritted dispersion tube. The gas flow was set at approximately 75 mL/min, thus maintaining the CO_2 partial pressure in solution at ~0.97 atm, as estimated from pH measurements in pure water. The solution was pre-equilibrated with the CO_2 gas for 6 h or until a steady-state pH was reached. The dissolution experiment was initiated upon the addition of a weighed amount (~0.5 g) of the sized dolomite crystals to the reaction vessel. < 10% of the starting material was dissolved by the end of each experiment so that variations in surface area were estimated at < 14% and deemed to have a small influence on the measured rates. The pH was measured using a combination glass electrode (Radiometer® GK2491C) connected to a Radiometer® M84 pH/mV-meter (Radiometer Copenhagen PHM 84 Research pH Meter). The pH electrode was calibrated using three NIST-traceable buffers (Fisher Scientific; pH = 2.00, 4.00 and 7.00 at 25 °C), prior to and after each sample measurement. Aliquots (10 mL) of the reacting solution were taken at the beginning of the run and at ~24-h intervals over the next five days (total of 5 sampling intervals for each experiment, time intervals between samplings sometime differ because of statutory holidays and lock-down of the laboratories, see Appendix A-1). The aliquots were filtered through a 0.45 μm Millipore polycarbonate filter and acidified with 0.1 mL of 5 N HCl. Dissolved Ca, Mg, Fe and Mn were analyzed by AAS and Na by Atomic Emission Spectroscopy (AES). The detection limits were estimated at 0.04 mg/L for Ca, Mg, Fe, and Mn and 0.01 mg/L for Na. The pH of the reacting solution was noted at each sampling interval. The initial and final pH for all experiments are given in Appendix (Table A-1).

2.3. Experimental calculations

The pH and pCO_2 were used to calculate the carbonic acid speciation (carbonate and bicarbonate ion concentrations) of the reacting solutions at different time intervals, by simple iterative mathematical calculations. The thermodynamic constants used in the speciation and saturation calculations were taken from the WATEQ4F database file in the PHREEQC program provided by the USGS (Parkhurst and Appelo, 2011). The additive species and complexation constants considered in the equilibrium calculations are given in Table 2. The activity coefficients of charged species were estimated using an extended Debye-Hückel equation whereas those of neutral species were calculated according to: $\gamma = 10^{-0.5I}$ (Busenberg and

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