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Experimental determination of the solubility product of dolomite at 50–253 °C

Pascale Bénézeth [a,*], Ulf-Niklas Berninger [a,b], Nicolas Bovet [c], Jacques Schott [a], Eric H. Oelkers [a]

[a] *Géosciences Environnement Toulouse, GET – CNRS – IRD – OMP – Université de Toulouse, 14, Avenue Edouard Belin, 31400 Toulouse, France*

[b] *Dept. für Geo- und Umweltwissenschaften, Ludwig-Maximilians-Universität München, Theresienstr. 41, 80333 München, Germany*

[c] *Department of Chemistry, Nano-Science Center, University of Copenhagen, Universtitetsparken 5, 2100 Copenhagen, Denmark*

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Abstract

The ‘dolomite problem’, the scarcity of present-day dolomite formation near the Earth’s surface, has attracted much attention over the past century. Solving this problem requires having reliable data on the stability and kinetics of formation of this mineral. Toward this goal, the solubility of natural dolomite ($CaMg(CO_3)_2$) has been measured from 50 to 253 °C in 0.1 mol/kg NaCl solutions using a hydrogen electrode concentration cell (HECC). The obtained apparent solubility products ($K_{app\text{-}sp\text{-}dol}$), for the reaction: $CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$, were extrapolated to infinite dilution to generate the solubility product constants for this reaction ($K_{sp^\circ\text{-}dol}$). The derived equilibrium constants were fit and can be accurately described by $\log_{10} K_{sp^\circ\text{-}dol} = a + b/T\ (\mathrm{K}) + cT\ (\mathrm{K})$ where $a = 17.502$, $b = -4220.119$ and $c = -0.0689$. This equation and its first and second derivatives with respect to T were used together with corresponding aqueous species properties to calculate the revised standard state thermodynamic properties of dolomite at 25 °C and 1 bar, yielding a Gibbs energy of formation ($\Delta_f G^\circ_{298.15}$) equal to -2160.9 ± 2 kJ/mol, ($\log_{10} K_{sp^\circ\text{-}dol} = -17.19 \pm 0.3$); an enthalpy of formation ($\Delta_f H^\circ_{298.15}$) of -2323.1 ± 2 kJ/mol, an entropy ($S^\circ_{298.15}$) of 156.9 ± 2 J/mol/K and heat capacity ($C^\circ_{p298.15}$) of 154.2 ± 2 J/mol/K (uncertainties are 3σ). The dolomite solubility product derived in this study is nearly identical to that computed using SUPCRT92 (Johnson et al., 1992) at 200 °C, but about one order of magnitude higher at 50 and 25 °C, suggesting that dolomite may be somewhat less stable than previously assumed at ambient temperatures.

Keywords: Dolomite solubility product; Thermodynamic properties; Stability

1. INTRODUCTION

Dolomite, $CaMg(CO_3)_2$, is a double carbonate in which Mg^{2+} and Ca^{2+} are segregated into separate planes of the crystal structure (Lippmann, 1973; Antao et al., 2004), with triangular CO_3^{2-} anion layers lying between the two cation layers. These anions layers are closer to Mg^{2+}, the smaller ion as shown in Fig. 1 (from Warren, 2000).

Dolomite is a common mineral in sedimentary rocks, ubiquitous in the past, yet rarely found in modern environments (Arvidson and Mackenzie, 1999; Mackenzie and Andersson, 2013). Cation ordered dolomite is challenging to synthesize under Earth surface conditions (Usdowski, 1994; Land, 1998) and its behavior, occurrence and uncertainties about its origin, a conundrum known as the “dolomite problem”, have attracted the attention of scientists for

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* Corresponding author.
E-mail address: pascale.benezeth@get.omp.eu (P. Bénézeth).

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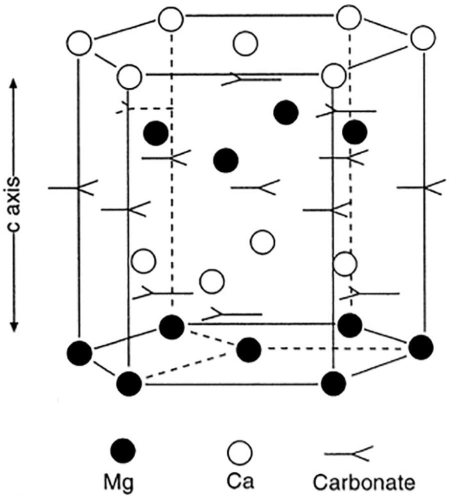

Fig. 1. Stoichiometric dolomite crystal structure showing the layers of carbonate ions separated by alternating layers of calcium and magnesium ions (after Warren, 2000).

more than two centuries (see Lippmann, 1973; Land, 1998; Arvidson and Mackenzie, 1999; Warren, 2000; Machel, 2004).

Understanding dolomite geochemistry and genesis through its solubility and stability is crucial to accurately model water–rock interactions (see e.g., Warren, 2000) in a large number of natural and geoengineered systems including (i) subsurface carbon storage (e.g. Oelkers et al., 2008; special issue Bénézeth et al., 2009 (Eds.) and papers therein; Snaebjornsdottir et al., 2017), (ii) dolomite reservoirs for hydrocarbon and natural gas exploration and recovery (e.g. Davies and Smith, 2006), (iii) hydrothermal alteration systems (e.g. Perkins, 1984; Machel and Lonnee, 2002), (iv) weathering processes and the global C cycle (e.g. Berner et al., 1983; Burns et al., 2000; Berner, 2004), and (v) to unravel the mysteries of dolomite formation at low temperatures (e.g. Arvidson and Mackenzie, 1999; Burns et al., 2000). Indeed, due to the difficulty of precipitating dolomite in the laboratory, questions surrounding its crystallinity, and other experimental challenges including controlling experimental CO_2 partial pressure and the measurement of pH and alkalinity above ambient temperatures, there is a wide disparity in the values of the dolomite solubility product reported in the literature at near to ambient temperatures. To resolve this disparity and owing to the scarcity of data at super-ambient temperatures, this study has been designed to (i) determine the solubility product of a natural dolomite at temperatures from 50 to 253 °C, (ii) verify its congruent/incongruent dissolution and reversibility, (iii) generate an improved, revised set of consistent thermodynamic properties and (iv) assess the quality of currently existing dolomite solubility data and estimates.

2. SUMMARY OF PAST WORK

Dolomite dissolution can be described by the reaction:

$$\mathrm{CaMg(CO_3)_2} = \mathrm{Ca^{2+}} + \mathrm{Mg^{2+}} + 2\mathrm{CO_3^{2-}} \qquad (1)$$

The law of mass action for reaction (1) can be written:

$$K_{sp^\circ-dol} = a_{Ca^{2+}} a_{Mg^{2+}} \left(a_{CO_3^{2-}}\right)^2 \qquad (2)$$

where $K_{\text{sp°-dol}}$ denotes the solubility product of dolomite and a_i refers to the activity of the subscripted aqueous species at equilibrium. Given the variety of experimental challenges mentioned in the introduction, previous studies of dolomite dissolution do not yield consistent and reliable solubility products. For example, the $\log_{10} K_{\text{sp°-dol}}$ values obtained at 25 °C range from −16.5 to −19.35 (see Table 1, Yanat'yeva, 1952; Kramer, 1959; Garrels et al., 1960; Langmuir, 1964; Halla and Van Tassel, 1965; Sherman and Barak, 2000). Yanat'eva (1952) reported a $\log_{10} K_{\text{sp°-dol}}$ of −18.37 at 25 °C, measured from dolomite dissolution experiments performed in pure water over 100 days. Garrels et al. (1960) performed dissolution experiments with dolomite in pure water at 25 °C and 1 atm pCO_2 for 18 h. The pH of the aqueous solution in equilibrium with <0.1 mm dolomite grains was 5.68 ± 0.02. These results yield a $\log_{10} K_{\text{sp°-dol}}$ value of −19.34. Garrels et al. (1960), however, reported that adding well-ground dolomite powder to their experimental solutions when they were close to the equilibrium pH of ~5.6 resulted in the rapid increase of pH to 6.2. The dissolution of fine-grained particles of greater solubility, or metastable phases generated during grinding, yields a $\log_{10} K_{\text{sp°-dol}}$ value of −16.44. Langmuir (1964) performed dolomite dissolution experiments in distilled water and dilute $MgCl_2$ solutions and reported a $\log_{10} K_{\text{sp°-dol}}$ value of −17.0, whereas Halla and Van Tassel (1965) reported a $\log_{10} K_{\text{sp°-dol}}$ of −17.76 at 21 °C from experiments performed in an initially pure water at 1 bar pCO_2. More recently, Sherman and Barak (2000) performed dolomite dissolution experiments at 25 °C and in aqueous Ca–Mg–HCO_3/CO_3 solutions lasting almost 2 years and derived a mean $\log_{10} K_{\text{sp°-dol}}$ value of -17.2 ± 0.2, in agreement with the value ($\log_{10} K_{\text{sp°-dol}} = -17.12$) that can be calculated using the thermodynamic properties of dolomite reported by Robie et al. (1978) when combined with the thermodynamic data of the aqueous species involved in reaction (1) as reported in Table 2. Most of the $\log_{10} K_{\text{sp°-dol}}$ values compiled in Table 1 are plotted as a function of the reciprocal temperature in Fig. 2, together with values generated from SUPCRT92, a software package used to calculate the equilibrium constants of reactions as a function of temperature (Johnson et al., 1992). It can be seen from this figure that the $\log_{10} K_{\text{sp°-dol}}$ values at 25 °C reported by Halla and Van Tassel (1965) and Yanat'eva (1952) fall among a group of values near −17.00 (Kramer, 1959; Langmuir, 1964; Robie et al., 1978; Sherman and Barak 2000), whereas that generated from SUPCRT92 (Johnson et al., 1992: $\log_{10} K_{\text{sp°-dol}} = -18.15$) and by Navrotsky and Capobianco (1987) from HCl solution calorimetry experiments performed at 85 °C ($\log_{10} K_{\text{sp°-dol}} = -18.2$ at 25 °C) are somewhat lower. The SUPCRT92 database uses dolomite thermodynamic data from Helgeson et al. (1978) to calculate the equilibrium constant. These data are based on the phase equilibrium for the reaction: