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Experimental determination of calcite solubility and the stability of aqueous Ca– and Na–carbonate and –bicarbonate complexes at 100–160 °C and 1–50 bar pCO_2 using *in situ* pH measurements

A.Yu. Bychkov [a], P. Bénézeth [b,*], O.S. Pokrovsky [b,c,d], Yu.V. Shvarov [a], A. Castillo [b], J. Schott [b]

[a] *Lomonosov Moscow State University, 1 Leninskie Gory, Moscow 119899, Russia*
[b] *Géosciences Environnement Toulouse (GET), Université de Toulouse, CNRS, IRD, OMP, 14 Avenue Edouard Belin, 31400 Toulouse, France*
[c] *Institute of Ecological Problems of the North, Federal Center of Arctic Research, 23 Nab. Severnoi Dviny, Arkhangelsk, Russia*
[d] *BIO-GEO-CLIM Laboratory, Tomsk State University, 35 Lenina, Tomsk, Russia*

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Abstract

The solubility of calcite was measured at 100, 120, 140 and 160 °C at 1–50 bar pCO_2 in 10^{-3}–0.1 $mol\cdot kg^{-1}$ NaCl solutions using a new experimental setup involving *in situ* pH measurements with high-temperature solid-contact H-selective glass and two types of reference electrodes: (*i*) Ag/AgCl in 3.5 M KCl, saturated AgCl placed in a Teflon extensible container with liquid junction, and (*ii*) solid-contact high-T Na-selective glass electrode in the cell without liquid junction. The stability constants of $NaHCO_3°$ and $NaCO_3^-$ aqueous complexes formation were determined in $NaCl$-Na_2CO_3/$NaHCO_3$ solutions in CO_2-free media and under 10 bar pCO_2 from 100 to 160 °C. These values allowed calculation of the pH of the calibration solution in the system $NaCl$-CO_2-H_2O used in the cell without liquid junction with Na^+-selective electrode as a reference. This highly stable, low-cost electrode system can be recommended for routine pH measurements at $4 < pH < 10$ in sodium-bearing solutions up to 160 °C and the critical point of CO_2. The values of the stability constants of $CaCO_3°$ and $CaHCO_3^+$ aqueous complexes and calcite solubility product were generated at 100, 120, 140 and 160 °C allowing a description of the solubility of calcite in a wide range of pH and pCO_2.

Keywords: Calcite; pH; High temperature; pCO_2; Carbonate; Solubility

1. INTRODUCTION

The reduction of CO_2 emissions to the atmosphere is one of the main challenges of this century. To reduce or at least slow down the atmospheric CO_2 concentration, the geologic sequestration of CO_2 seems quite promising due to the large storage capacity and geographic ubiquity of deep geological formations (e.g. Bachu et al., 1994; Holloway, 2001; Oelkers and Schott, 2005; Bénézeth et al., 2007, 2009a). Mineral trapping, which involves the incorporation of CO_2 into a solid phase, for example via the precipitation of carbonate minerals, is a safer way of CO_2 storage compared to solubility trapping in saline aquifers, for instance. Its modelling, in turn, requires knowing the thermodynamic parameters of the main carbonate

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* Corresponding author.
E-mail addresses: bychkov@geol.msu.ru (A.Yu. Bychkov), pascale.benezeth@get.omp.eu (P. Bénézeth).

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minerals and especially calcite and the Ca aqueous species present in the fluids resulting from CO_2 injection. Although a large amount of work has been devoted to the calcite-water system at ambient conditions, the thermodynamics of this system, including the stability constants of the aqueous $CaCO_3°$ and $CaHCO_3^+$ complexes, remain poorly characterized at elevated temperatures and pCO_2 pressures most pertinent to CO_2 geological sequestration. Moreover, although sodium chloride is considered as the main component of deep geological fluids, the stability of sodium-carbonate and bicarbonate complexes has been mostly investigated at room temperature and their extrapolation to elevated temperatures is not straightforward. Only the recent study of Stefánsson et al. (2013) has determined the parameters of these complexes to 200 °C.

The solubility of calcite has been thoroughly investigated. Starting from Engel (1889), many researchers conducted solubility experiments at both room temperatures (e.g., Leather and Sen, 1910; Kendall, 1912; Johnston, 1915; Frear and Johnston, 1929; Greenwald, 1941; Martynova et al., 1974, 1989; Millero et al., 1984) and super-ambient temperatures (Miller, 1952; Ellis, 1959, 1963; Segnit et al., 1962; Malinin and Kanukov, 1972; Plummer and Busenberg, 1982; Wolf et al., 1989). In contrast, the stability constants of the aqueous Ca hydroxo-carbonate complexes have been mostly investigated at room temperatures (i.e., Hopkins and Wulff, 1965; Nakayama, 1968; Lafon, 1970; Dyrssen and Hansson, 1973; Reardon and Langmuir, 1974) with only few measurements up to 90 °C (Plummer and Busenberg, 1982). To determine the distribution of the Ca aqueous species in equilibrium with calcite one has to know the solution pH value in addition to the total Ca concentration and pCO_2. pH measurements at temperatures above 100 °C are, however, technically challenging which explains why very few studies have been devoted to the temperature dependence of aqueous Ca-carbonate complexes stability. Using various modeling approaches, a number of authors found good agreement between calculated and measured calcite solubilities (Gal et al, 1996; Garcia et al., 2006). Yet, the mostly frequently used SUPCRT92 software packages that encode the revised-HKF equation of state (Johnson et al., 1992) and HCh code (Shvarov, 2008), yield large disagreements with the experimental result and as such require improvement of their thermodynamic database as shown below. Duan and Li (2008) attempted to calculate thermodynamic parameters and activity coefficients of solution components for description of calcite solubility up to 250 °C and 1000 bars. Based on available literature data, they calculated the Gibbs free energy of formation, enthalpy and entropy of $CaCO_3°(aq)$ and $CaHCO_3^+(aq)$, and suggested Pitzer parameters for activity coefficients.

Potentiometric measurements at elevated temperatures and partial CO_2 pressures allow determination of the solubility products of carbonate minerals as well as the formation constants of aqueous complexes under rigorous control of experimental parameters. There are only a few electrode systems that are capable of providing *in situ* pH values above 100 °C and pressures higher than saturated water pressures. The most reliable technique known today to measure the pH at hydrothermal conditions is the hydrogen electrode concentration cell (Palmer et al., 2001; Bénézeth et al., 2009b), which has been used to measure the solubility of various carbonate minerals (Bénézeth et al., 2007, 2009b, 2011, 2018; Lindner et al., 2018). The pH measurements in hydrothermal systems at temperatures above 300 °C are possible with an Y_2O_3-doped zirconia ceramic electrode (Lvov et al., 2003). A persistent problem is the high resistance of the zirconium electrode at low temperatures and the design of the reference electrode. The solid-contact glass electrode with special glasses developed to sustain both high pressures and temperature also has not been used widely (i.e., Pokrovski et al., 1995; Pokrovsky et al., 2009b). The key factor in the successful use of these glass electrodes is the reliability of the reference electrode system. The internal Ag/AgCl electrodes immersed in experimental Cl^- - containing solution cell without transfer were used for carbonate dissolution kinetics studies at temperatures below 100–150 °C and pCO_2 up to 55 bars (Pokrovsky et al., 2009a,b; Golubev et al., 2009). However, the stability of this electrode system at temperatures above 100 °C is quite poor due to the dissolution of the reference electrode components in the test solution. The systems with external reference electrode use a liquid junction salt bridge with the flow direction from the reactor to the external media (Pokrovski et al., 1995). An alternative system of liquid junction electrodes employs the injection of electrolyte in the reactor via a high-pressure pump (Reukov and Zotov, 2006; Tagirov et al., 2007). However, the large difference in pressure and temperature between the internal solution and the external reservoir requires a high flux of the electrolyte to the system, which limits the wide use of such devices, especially for long-term solubility or kinetic measurements. Spectrophotometric pH determination using indicators (such as 2-napthol/4-nitrophenol) that are thermally stable has been used recently to determine the first and second ionization constants of carbonic acid and the ion pair formation constants for $NaHCO_3°_{(aq)}$ and $NaCO_3^-{}_{(aq)}$ up to 200 °C (Stefánsson et al., 2013) as well as the formation constants for $MgHCO_3^+{}_{(aq)}$ and $MgCO_{3(aq)}$ up to 150 °C (Stefánsson et al., 2014). This technique, however, requires the knowledge of the ionization constants of the indicators as well as their thermal stability.

The present study is devoted to the determination of calcite solubility at 100, 120, 140 and 160 °C and 1–50 bar pCO_2 in 10^{-3}–0.1 $mol\cdot kg^{-1}$ NaCl solutions. For this purpose, we used a glass sodium-selective electrode as a reference electrode in cells without liquid junction in solutions having constant sodium activity. These solid-contact, high pressure and high temperature electrodes are commercially available from various Russian companies (Potential®, Econix-Expert®) and are proven to operate in the circumneutral range of pH to temperatures and pressures up to 200–220 °C and 300–500 bars, respectively (Pokrovski et al., 1995; Zotov et al., 2006). The measurements of pH and pNa electrode potentials in the Na-Ca-Cl-CO_2-H_2O system using different buffer solutions up to 160 °C allowed the determination of the stability constants of the sodium and calcium carbonate and bicarbonate ion pairs.

2. EXPERIMENTAL METHODS

2.1. *In-situ* pH measurements using a pH/pNa – Ag/AgCl reference electrode

The solution pH was measured *in-situ* using a commercial solid contact Li-Sn alloy pH electrode coupled with a home-made Ag/AgCl reference electrode placed in an extensible Teflon container (called “silfon” below) filled with 3.5 M KCl and saturated with AgCl (Fig. 1). The outlet of the silfon had a 45 μm porous filter. Before filling up, the silfon was mechanically expanded such that, during its contraction, a flux of electrolyte from the silfon to the outside solution did not exceed 1 mL per day. This addition of electrolyte increased the salinity of the initial solution by no more than $0.003\ \mathrm{mol\cdot kg^{-1}}$ or 0.3–3%. After 3–5 days, the flux of electrolyte ceased and new filling of silfon was necessary. This electrode system allowed measuring the potential in the cell:

Sn-Cu, Li-Sn alloy | H^+-selective glass | test solution || 3.5 M KCl – AgCl/Ag

This electrode system had an $E°$ of $\leq$–2200 mV and was connected to a high input impedance, high resolution pH meter (Econix-Expert$^{(R)}$, Russia). The calibration of this system was performed using three buffer solutions: $0.01\ \mathrm{mol\cdot kg^{-1}}$ HCl + $0.1\ \mathrm{mol\cdot kg^{-1}}$NaCl, $0.1\ \mathrm{mol\cdot kg^{-1}}$ K-phthalate and $0.05\ \mathrm{mol\cdot kg^{-1}}$Na-tetraborate (Fig. A1 of the Electronic Annex A). The pH values of the calibration solutions were taken from Galster (1991). Fast Nernstian response was observed and electrode potentials exhibited sufficient stability to provide uncertainties of ±0.01 pH units at 25 °C and ±0.03–0.05 pH units at 150 °C. Between two subsequent calibrations, the electrode shift was less than 0.5 mV/day at 25 °C, 1 mV/day over 3 days at 60 °C, 2–3 mV/day at 100 °C and 3–5 mV/day at 150 °C. The experimental slope was close to the Nernstian one at each temperature. Since the potential of the Ag/AgCl electrode strongly depends on temperature, there is no isopotential point on this calibration plot (Fig. A1 of the Electronic Annex A). Instead, there is a range of pH values over which lines intersect at different temperatures. The cell potential weakly depends on temperature at pH from 6 to 9, which is convenient for studying carbonate equilibria.

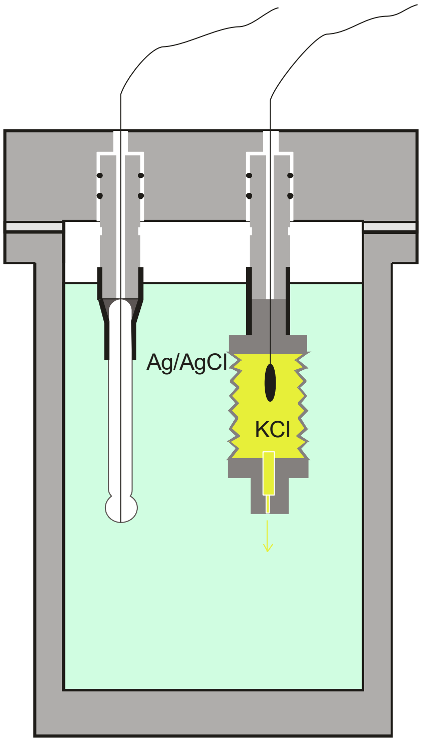

Fig. 1. Schematic illustration of the potentiometric cell used in the present study.

2.2. Calibration of the glass sodium-selective electrode

The following liquid-junction electrode system was used to calibrate the electrode:

Sn-Cu, Li-Sn alloy | Na^+-selective glass | test solution || 3.5 M KCl – AgCl/Ag

The calibration was performed in four NaCl solutions (0.001, 0.01, 0.1 and $1.0\ \mathrm{mol\cdot kg^{-1}}$) as illustrated in Fig. A2 of the Electronic Annex A. Na^+ activity in these solutions was calculated using the HCh code (Shvarov, 2008). To evaluate the effect of the liquid junction potential in this electrode cell, the silfon electrode was filled with KCl solutions of different concentrations (3, 4 and 5 M). We did not detect a change in cell potential among the different solutions within the precision of our measurements (±1 mV). Therefore, one can neglect the effect of diffusion and liquid junction potential in this system. The selectivity of the sodium electrode with respect to protons was tested in $0.1\ \mathrm{mol\cdot kg^{-1}}$ NaCl solutions at $4 \leq pH \leq 7$ and 140 °C (Fig. A3 of the Electronic Annex A). It can be seen that at pH < 4.3, the Na electrode potential increases due to competition with H^+ and thus this electrode is not suitable for pNa measurements at pH < 4.3.

2.3. Calibration of the pH electrode in cell without transfer with a Na-electrode as a reference

To calibrate the glass pH-electrode coupled with a Na-selective reference electrode, buffer solutions were prepared from sodium acetate and sodium carbonate having constant $Na^+(aq)$ activity of 0.08. The pH values of these solutions were calculated considering the complexation of sodium with acetate and carbonate ions (Fournier et al., 1998; and this work, respectively). Resulting pH values for each buffer solution are listed in Table A1. For comparison, the pH values measured directly by the pH-glass electrode are also listed in this table. A good agreement can be observed between the measured and calculated data. The differences between E_{pH} and E_{Na} depend only on pH and sodium activity. The direct measurement of these potentials thus provides a new reliable method for pH measurements in solutions having a constant activity of sodium ions in the cell without transfer:

Sn-Cu, Li-Sn alloy | H^+-glass | test solution | Na^+-glass | Sn-Cu, Li-Sn alloy.

The calibration curve is presented in Fig. A4 of the Electronic Annex A. The slopes of the calibration lines are close to theoretical Nernst slopes, both reported in Table A1. Using a cell with two glass electrodes provides reliable pH measurements over several days under high temperature and pressure. The maximum operating temperature of the cell is limited by the tin alloy melting point (~200 °C) and the stability of the glass membrane itself. In the circumneutral pH range of our experiments, the glass remained stable for more than 6 days at 140 °C, but its corrosion rate increased at 160 °C.

2.4. Experimental measurement of calcite solubility

Pure Prolabo calcite having a surface area of $0.38\ m^2 \cdot g^{-1}$ and a grain size of 10–50 µm (Pokrovsky et al., 2009b) was used for the solubility experiments. The powder (~20 grams) was placed in a titanium 450-mL Parr reactor continuously stirred by a magnetically driven Parr stirrer. Measurements of pH in experiments carried out in pure water were conducted using a cell with transfer:

Sn-Cu, Li-Sn alloy | H-selective glass | test solution || 3.5 M KCl – AgCl/Ag,

whereas, for experiments in $0.1\ mol \cdot kg^{-1}$ NaCl, pH measurements were performed with a cell without transfer:

Sn-Cu, Li-Sn alloy | H^+-glass | test solution | Na^+-glass | Sn-Cu, Li-Sn alloy

The reacting fluid was sampled through a porous 2 µm Ti filter using a manual Ti valve. Experiments were performed at 100, 120, 140 and 160 °C and 1–50 bar pCO_2. Typical time for achieving equilibrium did not exceed 2 hours as verified by preliminary kinetic experiments (Fig. A7).

2.5. Analyses

All input and output solutions were analyzed for total dissolved calcium ([Ca]), alkalinity ([Alk]), and pH as a function of time. Calcium was measured by flame atomic absorption with an uncertainty of ±1% and a detection limit of $7 \cdot 10^{-8}\ mol \cdot kg^{-1}$. Alkalinity was determined following a standard HCl titration procedure with an uncertainty of ±2% and a detection limit of $5 \cdot 10^{-5}\ mol \cdot kg^{-1}$.

2.6. Thermodynamic calculations

We used the HCh software package (Shvarov, 1981, 2008; Shvarov and Bastrakov, 1999), employing algorithms of free energy minimization. This code uses the Unitherm thermodynamic database containing Gibbs free energies of the simple ions, some polyatomic ions, and aqueous complexes, which are calculated according to the revised Helgeson-Kirkham-Flowers equations of state (HKF) (Helgeson et al., 1981; Tanger and Helgeson, 1988; Shock et al., 1992). Activity coefficients of all ions were computed using the Helgeson B-dot equation (Helgeson, 1969) with parameters from Shvarov and Bastrakov (1999). The CO_2 fugacity coefficient was calculated following the Peng-Robinson equation of state (Shvarov and Bastrakov, 1999) which agrees with the values of Spycher and Reed (1988). To insure the consistency of calculations in the H_2CO_3-H_2O system, we calculated the apparent dissociation constants of carbonic acid (Q_1, Q_2) in 0.2 m NaCl solution at 50–200 °C, using the thermodynamic parameters of Patterson et al. (1982, 1984). The agreement was within 0.01–0.04 log units, except for the calculated Q_1 at 150 and 200 °C where the HKF evaluation was 0.09 and 0.14 log units lower, respectively. The aqueous species and solid component HKF parameters in the $CaCO_3$-H_2O system were taken from the Slop07 database (Shock and Helgeson, 1988; Shock and Koretsky, 1995; Shock et al., 1997; Sverjensky et al., 1997; Geopig, 2010).

3. RESULTS

3.1. Determination of sodium-carbonate and sodium-bicarbonate stability constants at 100–160 °C

To use the Na^+-selective electrode as a reference for studying carbonate systems, the complexation of the sodium ion with carbonate and bicarbonate ions and other solution constituents should be taken into account. There are four major complexation reactions for Na^+(aq):

$$Na^+ + HCO_3^- = NaHCO_3^\circ \quad K_{NaHCO_3^\circ} = \frac{a_{NaHCO_3^\circ}}{a_{Na^+} a_{HCO_3^-}} \tag{1}$$

$$Na^+ + CO_3^{2-} = NaCO_3^- \quad K_{NaCO_3^-} = \frac{a_{NaCO_3^-}}{a_{Na^+} a_{CO_3^{2-}}} \tag{2}$$

$$Na^+ + Cl^- = NaCl^\circ \quad K_{NaCl^\circ} = \frac{a_{NaCl^\circ}}{a_{Na^+} a_{Cl^-}} \tag{3}$$

$$Na^+ + OH^- = NaOH^\circ \quad K_{NaOH^\circ} = \frac{a_{NaOH^\circ}}{a_{Na^+} a_{OH^-}} \tag{4}$$

where a_i and K_i stand for the activity and stability constant of the *ith* aqueous species or complex, respectively. The stability constants of the sodium chloride complex (reaction (3)) were determined in a wide range of temperature using conductivity techniques (Quist and Marshall, 1969). The stability constants of the NaOH°(aq) complex (reaction (4)) were also studied at high temperature by Ho et al. (2000) and Fuangswasdi et al. (2000). In contrast and until recently, sodium-carbonate and -bicarbonate complexes (reactions (1) and (2)) were studied only at room temperatures, reviewed in the study of Stefánsson et al. (2013) who measured the carbonic acid ionization and the stability of sodium bicarbonate and carbonate ion pairs up to 200 °C using potentiometric and spectrophotometric approaches.

In the present study, the stability constants were determined using an isothermal cell with transfer operating simultaneously with two electrode systems:

Table 1
Logarithm of the calculated experimental values of the equilibrium constants for reactions (1), (2), (5), (6) and (7) and calcite solubility product determined in this study.

Reaction	100 °C	120 °C	140 °C	160 °C
(1) $Na^+ + HCO_3^- = NaHCO_3^\circ(aq)$	0.19 ± 0.10	0.31 ± 0.10	0.36 ± 0.10	0.47 ± 0.20
(2) $Na^+ + CO_3^{2-} = NaCO_3^-(aq)$	1.72 ± 0.20	1.88 ± 0.20	1.94 ± 0.20	2.10 ± 0.20
(5) $Ca^{2+} + HCO_3^- = CaHCO_3^+$	1.53 ± 0.10	1.66 ± 0.05	1.87 ± 0.10	2.25 ± 0.20
(6) $Ca^{2+} + CO_3^{2-} = CaCO_3^\circ(aq)$		4.46 ± 0.03	4.75 ± 0.06	5.06 ± 0.10
(7) $CaCO_3(s) + 2H^+ = Ca^{2+} + H_2O(l) + CO_2(g)$	8.92 ± 0.05	8.79 ± 0.03	8.70 ± 0.10	8.62 ± 0.20
$CaCO_3(s) = Ca^{2+} + CO_3^{2-}$	−9.45 ± 0.05	−9.81 ± 0.03	−10.09 ± 0.10	−10.53 ± 0.20

Sn-Cu, Li-Sn alloy | Na^+-selective glass | test solution ‖ 3.5 M KCl – AgCl/Ag,
Sn-Cu, Li-Sn alloy | H-selective glass | test solution ‖ 3.5 M KCl – AgCl/Ag

Four tests solutions having constant ionic strength of 0.1 and 1.0 were used (0.9 mol·kg^{-1} NaCl + 0.05 mol·kg^{-1} Na_2CO_3; 0.6 mol·kg^{-1} NaCl + 0.2 mol·kg^{-1} Na_2CO_3; 0.5 mol·kg^{-1} Na_2CO_3; 0.1 mol·kg^{-1} NaCl). The electrode

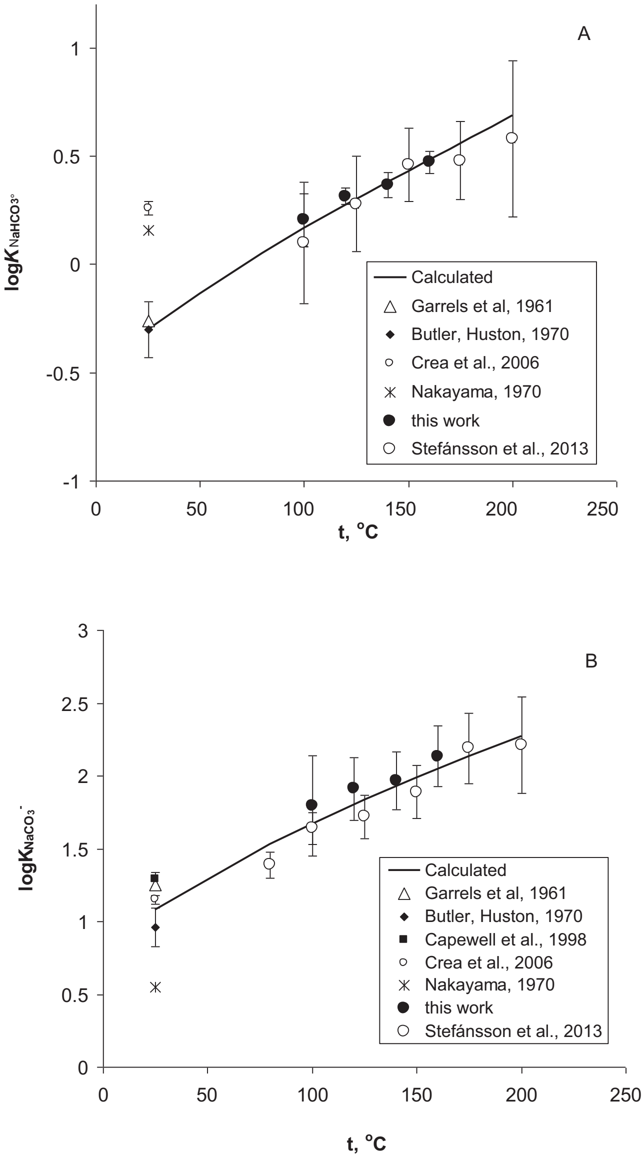

Fig. 2. The temperature dependence of log $K_{NaHCO_3^\circ}$ (A) and log $K_{NaCO_3^-}$ (B). Calculated line by Stefánsson et al. (2013). (See above-mentioned references for further information.)

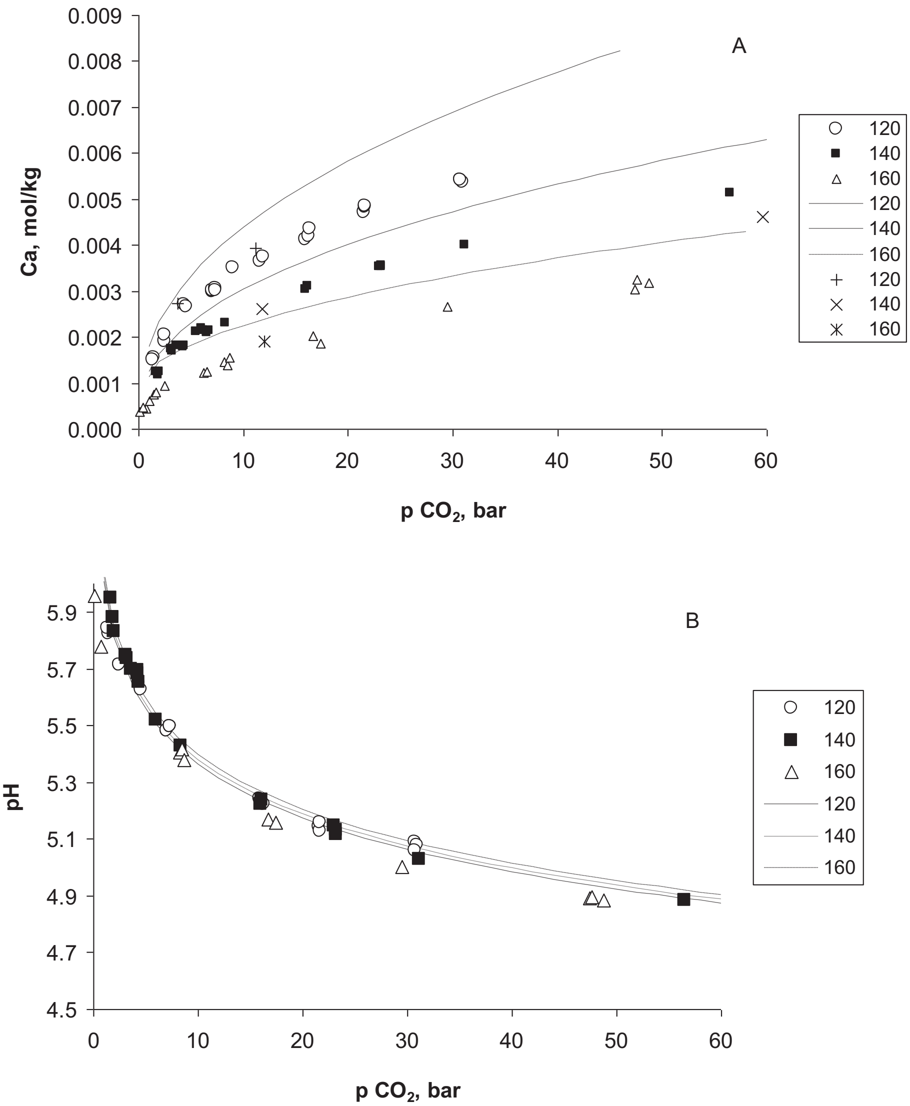

Fig. 3. Calcite solubility (A) and pH (B) as a function of pCO_2 in pure water. Lines represent the calculation using Slop07 database (Geopig 2010, http://geopig.asu.edu/). Cross symbols represent Ellis (1959) data.

cell potential in solutions having different Na_2CO_3 molalities is illustrated in Fig. A5 of the Electronic Annex A, and the results of the calculations of $NaCO_3^-$ stability constant in the different buffer solutions are listed in Table A2 of the Electronic Annex A. The study of the Na^+ - bicarbonate ion pair stability was performed in three buffer solutions with a constant CO_2 partial pressure of 10 bars ($0.9\ mol \cdot kg^{-1}$ NaCl + $0.05\ mol \cdot kg^{-1}$ Na_2CO_3; $0.6\ mol \cdot kg^{-1}$ NaCl + $0.2\ mol \cdot kg^{-1}$ Na_2CO_3; $1\ mol \cdot kg^{-1}$ $NaHCO_3$). The dependence of the electrode cell potential on sodium bicarbonate molality is illustrated in Fig. A6, and the results of the calculation of $NaHCO_3°$ stability constants are reported in Table A3 of the Electronic Annex A.

To calculate the $NaHCO_3°$ and $NaCO_3^-$ stability constants from our measurements, activity coefficients of all ions were computed using the Helgeson B-dot equation (Helgeson, 1969). All calculations were performed using the HCh computer code (Shvarov, 2008) and the Gibbs free energies of formation of sodium – carbonate and bicarbonate complexes were derived from the obtained constants. The calculated values of $\log K_{NaHCO_3°}$ and $\log K_{NaCO_3^-}$ are reported in Table 1, and plotted as a function of temperature in Fig. 2 together with literature data. The values obtained in this study are in excellent agreement with the experimental values reported by Stefánsson et al. (2013). The determination of $NaHCO_3°$(aq) and $NaCO_3^-$(aq) stability constants allowed precise calculation of the pH values of the carbonate buffer solutions and produced a practical (operational) scale of pH measurement using the sodium-selective electrode as a reference in the cell without transfer.

3.2. Calcite solubility

The results of calcite solubility measurements in pure water at 120, 140 and 160 °C as a function of pCO_2 are shown in Fig. 3 and listed in Table A4 of the Electronic

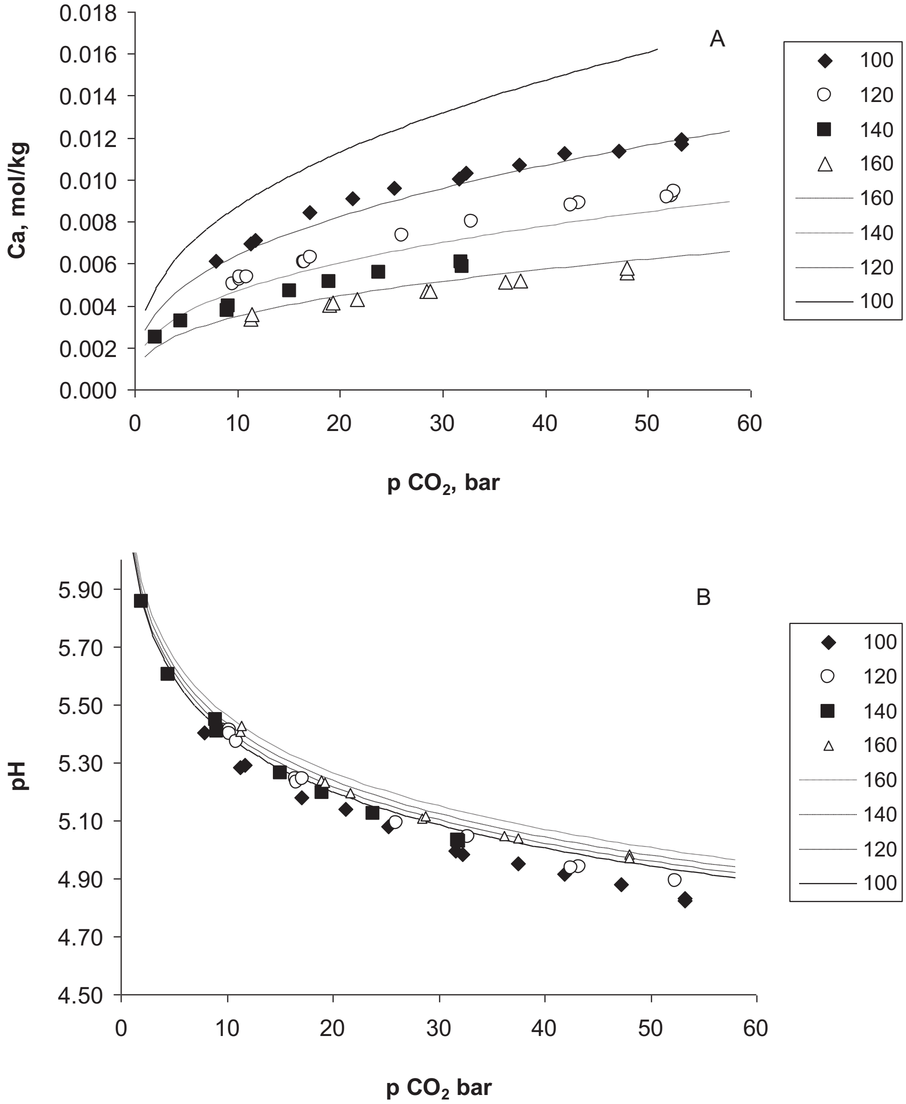

Fig. 4. Calcite solubility (A) and pH (B) as a function of pCO_2 in 0.1 mol·kg^{-1} NaCl. Lines represent the calculation using Slop07 database. See the text.

Annex A. It can be seen that the solubility of calcite in pure water increases with pCO_2 and decreases with temperature, in agreement with the data of Ellis (1959) as shown in Fig. 3A. Since Ellis (1959) did not use a uniform temperature step in his experiments, we reported in Fig. 3A the results he obtained at the temperatures closest to those investigated in the present study (120, 140, 160 °C). Prediction of calcite solubility using the Slop07 database (Geopig, 2010) significantly overestimates the calcite solubility measured in the present study. It should be noted that our measured pH values are the same within uncertainties as those calculated using Slop07 (see Fig. 3B). This suggests that the discrepancy between measured and calculated calcite solubility arises from the values of HKF parameters of Ca aqueous species in the Slop07 database.

Results of calcite solubility in 0.1 mol·kg^{-1} NaCl are listed in Table A5 of the Electronic Annex A and illustrated in Fig. 4A. As in the case of calcite solubility in pure water, calculations by the HCh software using the parameters in the slop07 database, together with activity coefficients calculated with the B-dot equation, overestimate calcite solubility in 0.1 mol·kg^{-1} NaCl, especially at $T \leq 140$ °C. In addition, calculated pHs with Slop07 database systematically overestimate the experimental pH values at all temperature (Fig. 4B).

Results of calcite solubility measurements in Na_2CO_3 solutions without CO_2 pressure are illustrated in Fig. 5 and the raw experimental data are listed in Table A6 of the Electronic Annex A. It can be seen that there is no dependence of calcite solubility on Na_2CO_3 concentration up to 0.2 mol·kg^{-1} Na_2CO_3.

4. DISCUSSION: THERMODYNAMIC MODELING

The thermodynamic properties of calcite are well known (Bäckström, 1925; Robie et al., 1978; Garrels and

Thompson, 1962; Plummer and Busenberg, 1982). The thermodynamic parameters of Ca^{2+}(aq) are based on the enthalpy of CaO dissolution (Thorvaldson et al., 1929) and the temperature dependence of calcite solubility product (Reardon and Langmuir, 1974). The HKF parameters for Ca^{2+} originate from Shock and Helgeson (1988).

The first main result of the present study is that the HKF model with the Slop07 database significantly overestimates calcite experimental solubility. This discrepancy increases with pCO_2 and temperature (Figs. 3 and 4). Therefore, we revised the calcite solubility product and the stability constants of calcium bicarbonate and carbonate complexes based on the new experimental data obtained in this study. From our experiments, we can define the total Ca concentration by taking into account the stability constants for the reactions below (5)–(9).

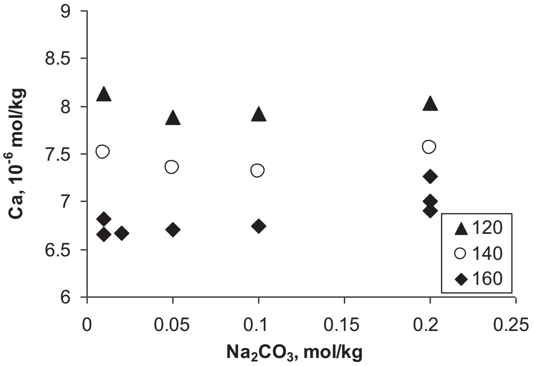

Fig. 5. Solubility of calcite in Na_2CO_3 solutions without CO_2.

$$Ca^{2+} + HCO_3^- = CaHCO_3^+ \quad K_{CaHCO_3^+} = \frac{a_{CaHCO_3^+}}{a_{Ca^{2+}}a_{HCO_3^-}} \tag{5}$$

$$Ca^{2+} + CO_3^{2-} = CaCO_3^\circ \quad K_{CaCO_3^\circ} = \frac{a_{CaCO_3^\circ}}{a_{Ca^{2+}}a_{CO_3^{2-}}} \tag{6}$$

The solubility of calcite can be expressed as:

$$[Ca]_T = [Ca^{2+}] + [CaHCO_3^+] + [CaCO_3^o]$$

where [i] stands for the molality of the *ith* aqueous species.

The reactions describing calcite solubility with their corresponding stability constants can be represented in the following way:

$$CaCO_3(s) + 2H^+ = Ca^{2+} + H_2O(l) + CO_2(g) \quad K_7 = \frac{a_{Ca^{2+}}P_{CO_2}}{a_{H^+}^2} \tag{7}$$

$$CaCO_3(s) + H^+ = CaHCO_3^+ \quad K_8 = \frac{a_{CaHCO_3^+}}{a_{H^+}} \tag{8}$$

$$CaCO_3(s) = CaCO_3^\circ \quad K_9 = a_{CaCO_3^\circ} \tag{9}$$

The total concentration of calcium in equilibrium with calcite is then given by:

$$[Ca]_T = \frac{K_7 a_{H^+}^2}{\gamma_2 P_{CO_2}} + \frac{K_8 a_{H^+}}{\gamma_1} + \frac{K_9}{\gamma_0} \tag{10}$$

where γ_0, γ_1, and γ_2 are the activity coefficients of neutral, singly-charged and divalent species, respectively. The value of K_9 (Eq. (9)) could be directly derived from calcite solubility in alkaline solutions as illustrated in Fig. 5 which presents calcite solubility in Na_2CO_3 solutions without added carbon dioxide. The logarithm of K_9 value was found to

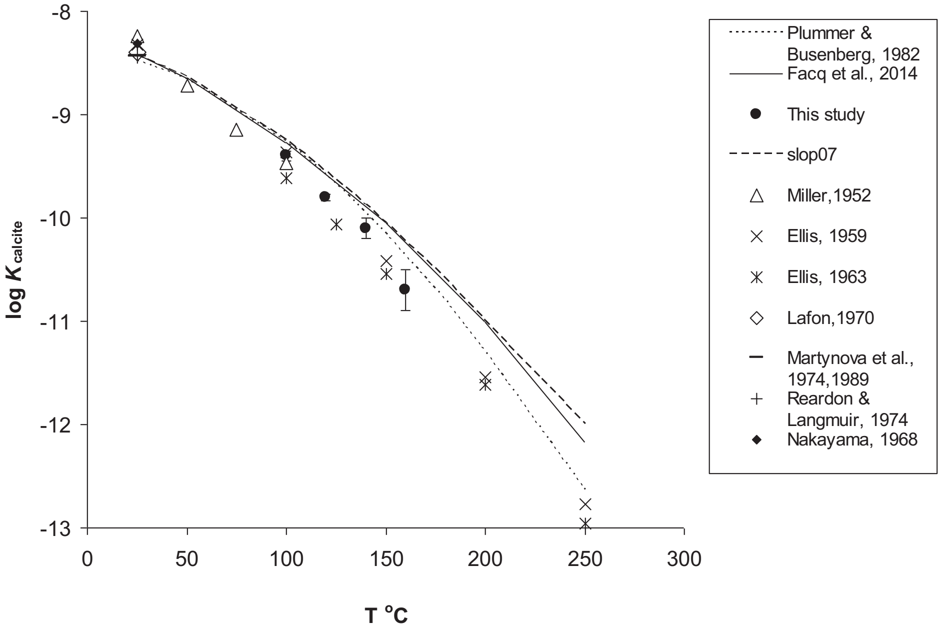

Fig. 6. The temperature dependence of the solubility product of calcite calculated from our experimental data (reported in Table 1) as well as the data from previous studies reported as symbols and predicted (lines) by (i) the Plummer and Busenberg (1982) equation, (ii) values generated using Slop07 database and the data of Shock et al. (1997) and Sverjensky et al. (1997), and (iii) Facq et al. (2014).

be equal to −5.10, −5.13, and −5.16 at 120, 140 and 160 °C, respectively. However, the precision of pH measurements at elevated temperatures is not sufficient to rigorously resolve Eq. (10) for K_7 and K_8. As such, we used a computer program OptimA to determine the thermodynamic parameters in the system. The program OptimA

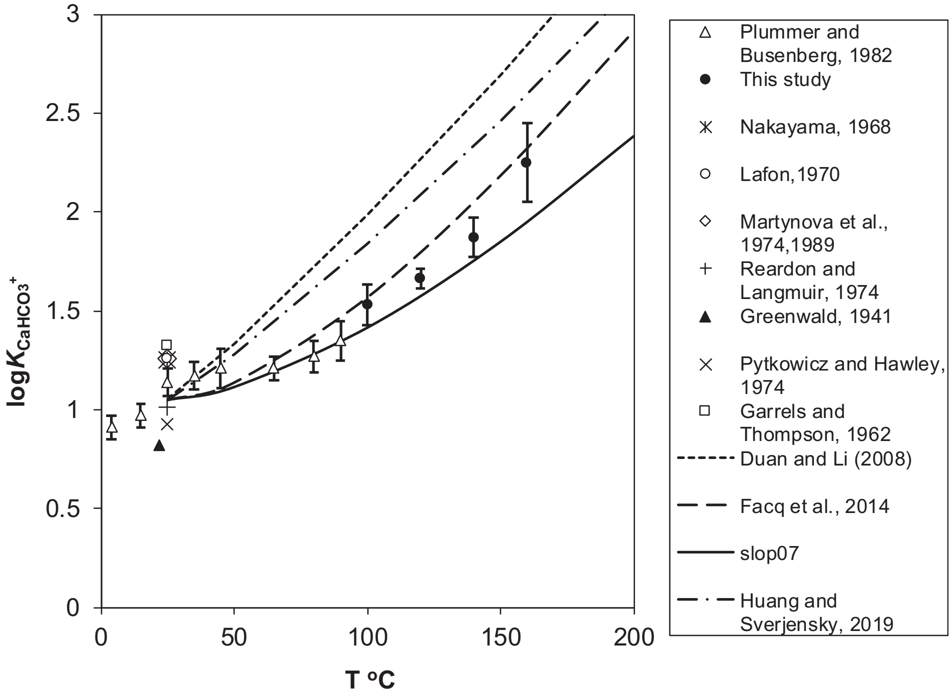

Fig. 7. The temperature dependence of the $CaHCO_3^+$ stability constant (Eq. (5)) from our experimental data as well as the data from previous studies reported as symbols and predicted (lines) by (i) Plummer and Busenberg (1982), (ii) Duan and Li (2008), (iii) values generated using Slop07 database and the data of Shock et al. (1997) and Sverjensky et al. (1997), (iv) Facq et al. (2014), and (v) Huang and Sverjensky (2019). (See above-mentioned references for further information)

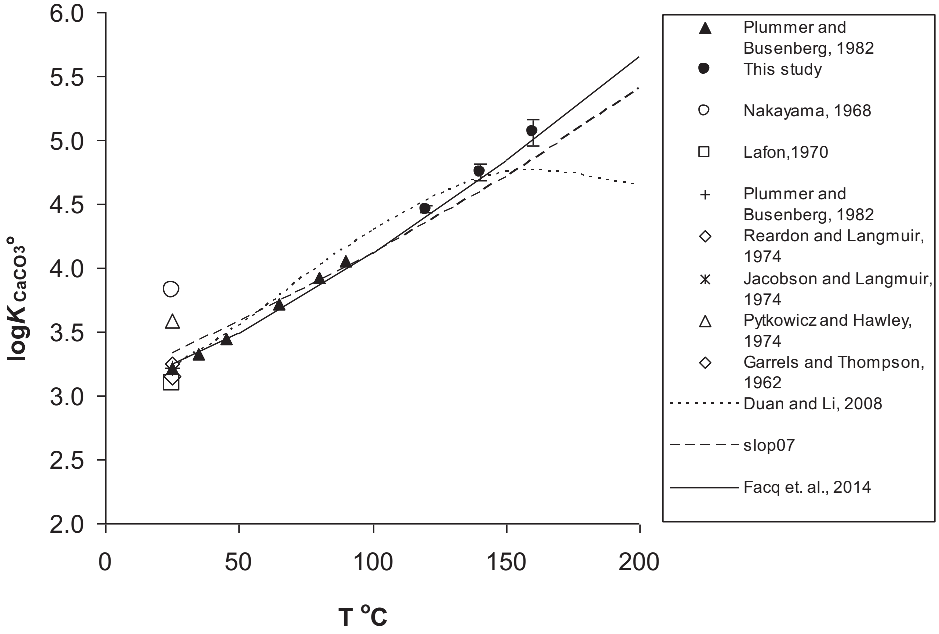

Fig. 8. The temperature dependence of the $CaCO_3°(aq)$ stability constant (Eq. (6)) from our experimental data as well as the data from previous studies reported as symbols and predicted (lines) by (i) values generated using Slop07 database and data of Shock et al. (1997) and Sverjensky et al. (1997), (ii) Duan and Li (2008) and (iii) Facq et al. (2014).

defines simultaneously at different temperatures the Gibbs free energies of a limited number of species in aqueous solutions based on experimental data using the HCh package for Windows (Shvarov, 2015). Details on operating the OptimA program and examples of calculations are given in the Electronic Annex B. To accurately define the Gibbs free energy of the calcium aquo ion and its carbonate and bicarbonate complexes, the program processed simultaneously all data on the solubility of calcite measured in the present work as a function of temperature and pCO_2 in pure water, 0.1 mol·kg^{-1} NaCl and Na_2CO_3 solutions listed in Table A4, A5 and A6 of the Electronic Annex A. The program adjusts the Gibbs free energy of formation of Ca^{2+}(aq) to provide the best fit of the full set of experimental data. The results of the calculations demonstrate that, in order to reproduce the solubility of calcite above 100 °C, one has to take into account the formation of Ca-bicarbonate complexes. The values of the formation constants of the sodium and calcium bicarbonate and carbonate complexes calculated based on our experimental data are listed in Table 1.

The temperature dependence of the calcite solubility product ($CaCO_3(s) = Ca^{2+} + CO_3^{2-}$) and the stability constants of $CaHCO_3^+$(aq) and $CaCO_3°$(aq) complexes, reported in Table 1, are depicted in Figs. 6, 7 and 8, respectively. These values are compared to the results of previous literature studies (reported as symbols in these figures) as well as prediction based on values extrapolated from the work of Plummer and Busenberg (1982), Duan and Li (2008), Facq et al. (2014), Huang and Sverjensky (2019) or using the HKF model with the Slop07 database (Shock and Helgeson, 1988; Shock and Koretsky, 1995; Shock et al., 1997; Sverjensky et al., 1997). The HKF parameters reported by Huang and Sverjensky (2019) and Facq et al. (2014) have been used here to recalculate the values log $K_{calcite}$, log $K_{CaHCO_3^+}$ and log $K_{CaCO_3°}$ using the HCh code

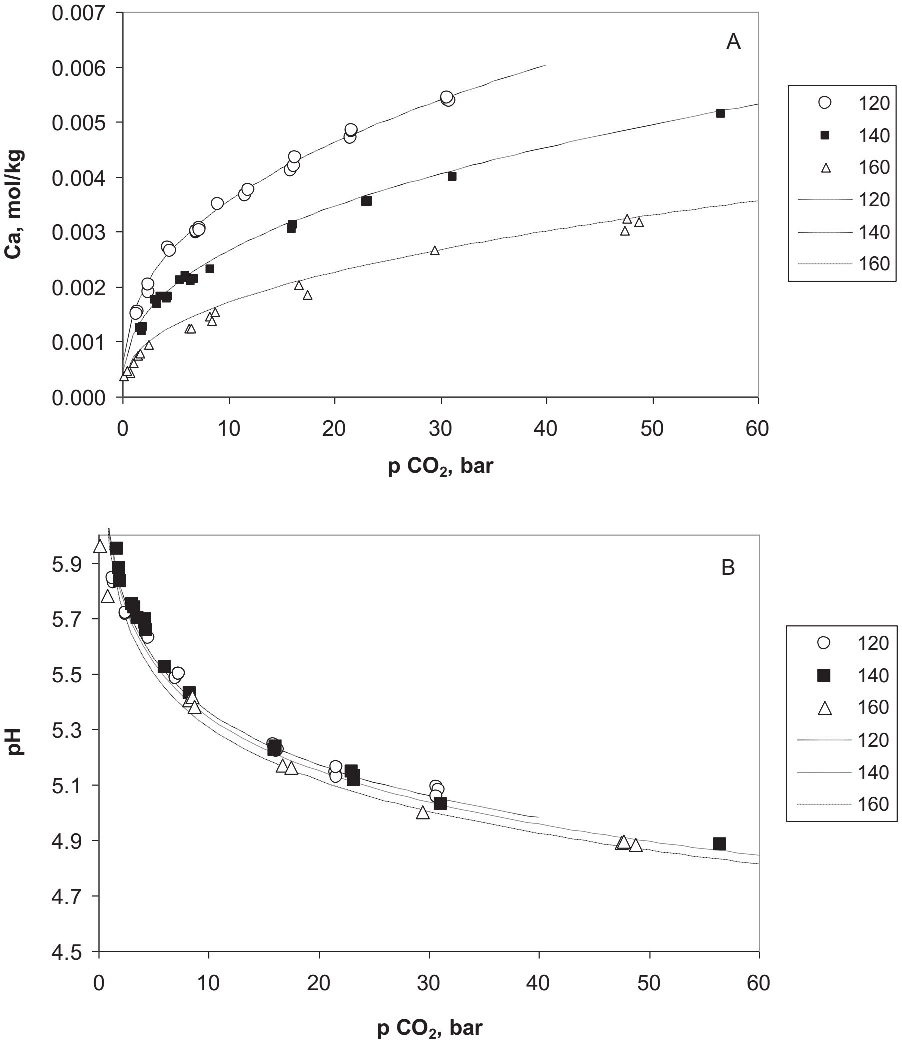

Fig. 9. Calcite solubility (A) and pH (B) as a function of pCO_2 in pure water. Lines represent calculations using new values for calcite solubility product ($CaCO_{3(s)} = Ca^{2+} + CO_3^{2-}$) and the stability constants of $CaHCO_3^+$(aq) and $CaCO_3°$(aq) complexes, reported in Table 1.

and Unitherm database (Shvarov, 2008) as plotted in Figs. 6–8. It can be seen that the values calculated from the data of Facq et al (2014) for the solubility product of calcite are almost identical to the predictions made using Slop07. However, their data are in very good agreement with our experimental values for log $K_{CaHCO_3^+}$ and log $K_{CaCO_3^\circ}$, which is not the case for the data generated from the revised data provided by Huang and Sverjensky (2019).

Based on the new values of calcite solubility product and $CaHCO_3^+$ and $CaCO_3°$ stability constants generated in the present study, we calculated calcite solubility (as total calcium concentration) and equilibrium pH in pure water and in 0.1 mol·kg^{-1} NaCl as a function of pCO_2 (Figs. 9 and 10, respectively). New recommended log K values (Table 1) allow an accurate description of experimental data at 100–160 °C within the uncertainty of measurements. Experimental pH values of 0.1 mol·kg^{-1} NaCl solutions in equilibrium with different partial pressure of pCO_2 at 120, 140 and 160 °C agreed (±0.1–0.2 pH units) with those calculated using the HCh code with implemented stability constants of $NaCO_3^-$ and $NaHCO_3°$ or those taken from Stefánsson et al. (2013) as illustrated Fig. 10B.

These results show that the proposed potentiometric setup with a pH electrode in a cell without transfer and a Na-electrode as a reference can be used in aqueous solutions where the activity of the sodium ion is known or can be calculated. This cell is highly stable and could be used, for example, to monitor pH in the ocean, groundwaters, soda lakes, and other natural environments with constant activity of sodium ion.

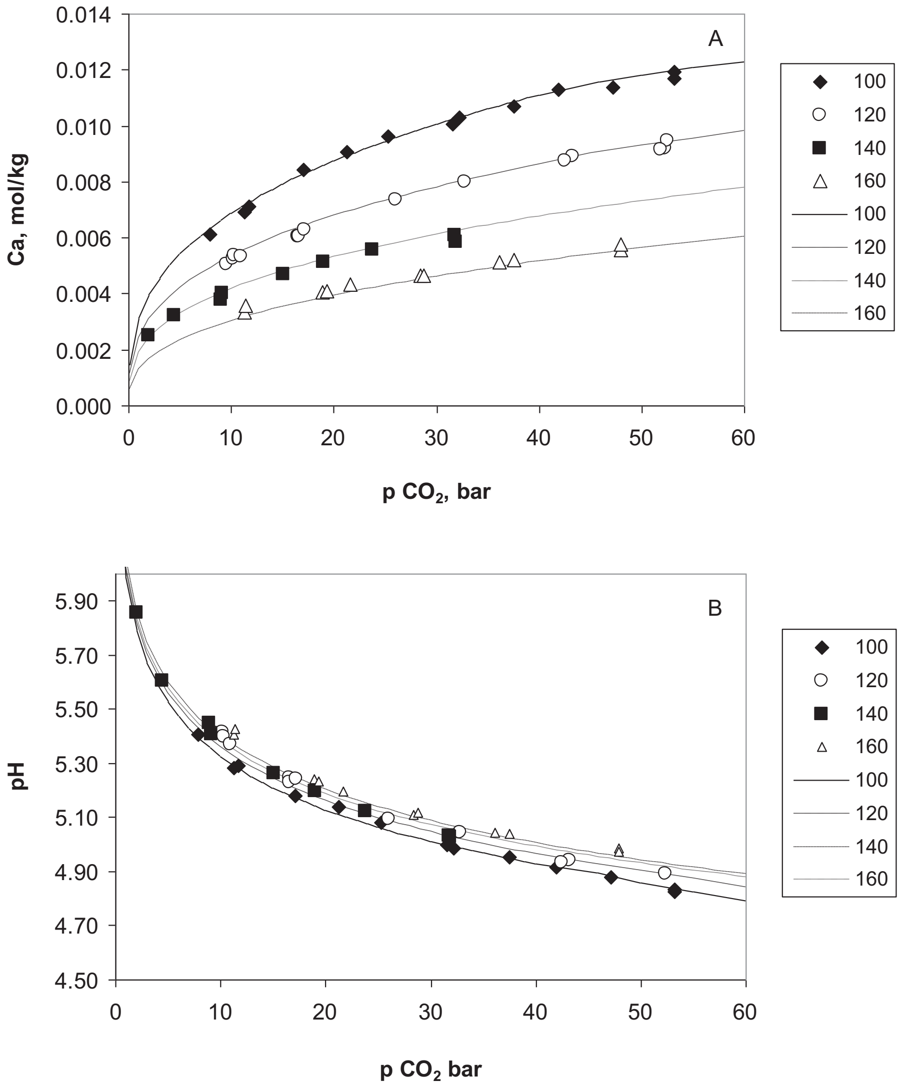

Fig. 10. Calcite solubility (A) and pH (B) as a function of pCO_2 in 0.1 mol·kg^{-1} NaCl. Lines represent results of calculations using new lvalues for calcite solubility product ($CaCO_{3(s)} = Ca^{2+} + CO_3^{2-}$) and the stability constants of $CaHCO_3^+$(aq), $CaCO_3°$(aq), $NaHCO_3°$(aq) and $NaCO_3^-$(aq) complexes, reported in Table 1.

5. CONCLUSIONS

The use of a solid-contact pH glass electrode coupled with Ag/AgCl/KCl (sat) liquid-junction reference electrode allows robust and precise measurement of pH in CO_2-H_2O systems up to 160 °C and 60 bar pCO_2. Conceptually new *in situ* pH-measurement system consisting of a pH-glass electrode and a reference Na^+ electrode (solid contact system without liquid junction) has been also described which allows continuous pH measurements in circumneutral and alkaline solutions with fixed activity of Na^+ ion. This electrode system was used to measure calcite solubility and to assess calcite solubility product and the stability of $CaCO_3°$, $CaHCO_3^+$ and $NaCO_3^-$ complexes at 100, 120, 140 and 160 °C and 1–50 atm pCO_2.

It is hoped that the new experimental sets-ups and the results of this study could renew the interest for modeling carbonate equilibria in low-temperature hydrothermal conditions to better understand serpentinization and other natural processes, and predict the consequences of CO_2 sequestration and storage efforts to overcome climate change. These data also could help in the modeling of the subsurface biosphere in continental and marine hydrothermal systems, deep sediments, and basement rocks on the seafloor.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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APPENDIX A. SUPPLEMENTARY MATERIAL

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