

Electronic Supplementary Information (METHODS & CALCULATIONS)

Preparation and standardization of titrant solutions

All solutions were prepared using analytical grade reagents and high purity deionized (Milli-Q[®], ~ 18 Mohm · cm) water. Hydrochloric acid solutions were prepared from 32% HCl and standardized using three gravimetrically prepared tris(hydroxymethyl)methylamine (TRIS) solutions that were kept refrigerated. The precision of this standardization was better than 0.1 %. The calcium titrant stock solutions and calcium standards were prepared from CaCl₂·H₂O crystals and kept refrigerated before use. These solutions were standardized by volumetric titration with EGTA.⁷⁷ The EGTA titrant solution was standardized using Copenhagen IAPSO standard seawater. The precision of this determination was better than 0.4 %.

Chemical analyses of CaCO₃ suspensions

Alkalinity measurements were carried out using a Radiometer TTT85 titration system with standardized HCl. The end-point of the titration was identified by the first-derivative method.⁷⁸ The precision of the analysis was better than ± 0.4% and the limit of detection was of 6 μmol kg⁻¹. Total calcium concentrations were measured by Flame Atomic Absorption Spectrophotometry (FAAS, AAnalyst 100TM 800 Perkin Elmer) using external standards (i.e., diluted from a 1000 ppm Certified Standard). The detection limit of this analysis was 3 μg L⁻¹ with a reproducibility of ± 5%. pH measurements were performed with a Schott N6980 pH combination electrode, suitable for concentrated suspensions, and calibrated against four NIST-traceable pH buffer solutions (4.01, 7.00, 10.00 and 11.00) at 25 ± 0.5°C with a precision of ± 0.02 pH units. Its Nernstian behavior was always very similar (59.2 ± 1.1 mV/decade to the theoretical value at 25°C. Calcium ion activities were measured with a combination Orion 97-20 ionplus[®] ion selective electrode calibrated with CaCl₂ standards (5·10⁻⁶ to 0.015 M) prepared in 0.02 M KCl solutions following the manufacturer's recommendation to achieve a precision of ± 4%. at 25 ± 1°C. Carbonate ion activities were determined using a combination ELIT Ion 8091 ion selective electrode initially calibrated by two methods: A) against NaHCO₃ standards prepared in 0.02 M KCl solutions, covering a relatively wide range of CO₃²⁻ ion concentrations (3·10⁻⁶ to 0.012 M) and B) against pre-equilibrated calcite suspensions prepared in 0.02 M KCl at different initial ΣCa: ΣHCO₃⁻: ΣCO₃²⁻ ratios (achieved with additions of CaCl₂, KHCO₃ and/or K₂CO₃) to cover a range of carbonate ion concentrations similar to the one of method A (2·10⁻⁶ to 0.008 M). In method A, CO₃²⁻ ion activities in the standards were estimated from thermodynamic equilibrium calculations performed iteratively using the Newton-Raphson method implemented in an in-house Matlab[®] subroutine using alkalinity and pH measurements as input. In contrast, in method B, CO₃²⁻ ion activities were estimated using the Ca²⁺ ion activities measured with the ISE in the equilibrated calcite suspensions, just before the calibration of the CO₃²⁻ ISE, and application of the solubility product relationship:

$$a_{CO_3^{2-}} = \frac{K_{sp}^0}{a_{Ca^{2+}}} \quad (R1)$$

where a represent the activity of the specified ion and K_{sp}^0 stands for the thermodynamic solubility product of calcite at 25°C. Method B provided better (Nernstian) and more reproducible calibration slopes and was, therefore, adopted for the routine calibration of the CO₃²⁻ ISE. Thermodynamic constants used in all calculations of this study are given in Table 1 in the main text. The optimum operational pH, temperature and analyte concentration ranges were respected for the three ISEs. Nevertheless, it must be noted that the CO₃²⁻ ISE only performed to specifications in a few preliminary titrations (see below). We suspect that the presence of CaCO_{3(s)} particles in our experiments may significantly decrease the operational life expectancy of this ISE. Consequently, this ISE was only used in preliminary titrations to validate the experimental protocol described below, estimate the re-equilibration time required after discrete titrant additions, evaluate titration system drift, and monitor the calcite saturation state. In all other experiments, CO₃²⁻ ion activities were derived from the Ca²⁺ ISE activities and application of Equation R1 (in analogy to the CO₃²⁻ ISE calibration by method B).

Calcite specimen

All titrations were carried out with Baker “Intra-analyzed flux reagent” grade calcium carbonate powder that was size-separated by settling through a 3 m x 0.1 m Plexiglas[®] tube filled with Milli-Q[®] water. The middle third portion of the settled CaCO₃ was freeze-dried and used for all experiments reported in this paper. The average grain size was estimated at 3-7 μm based on Stoke's Law and corroborated by numerous Scanning Electron Microscopy (SEM) images. X-ray diffraction and SEM analysis of this material confirmed that the powder was composed of at least 99% calcite. The specific surface area of the size-separated fraction was of 0.46 (± 0.02) m² g⁻¹, as determined by the multiple-point N₂-BET method⁷⁹ with an Autosorbed-1 Physisorption Analyzer. This parameter was determined before and after one acidimetric and one calcium titration to check for variations resulting from the dissolution of the finest particles and/or possible calcite re-precipitation. The specific surface area of the titrated solids was, within the uncertainty of our measurements, identical to the starting material, and therefore, the original value was used in further calculations. To minimize possible surface irregularities (such as step edges and kinks), a fraction of the calcite powder was aged in Milli-Q[®] water for about one year. This is a common procedure used in sorption studies to “heal” carbonate mineral surface defects (e.g., steps, dislocations, and point defects) and minimize the heterogeneity of surface site energies upon re-crystallisation.^{7,73,74} Furthermore, this pre-treatment, through Ostwald ripening, allows the dissolution of smaller CaCO₃ particles and re-precipitation onto larger particles, and hence, a narrowing of the particle size distribution.⁸⁰ Before use in surface titrations, the calcite powder was exhaustively rinsed with Milli-Q[®] water to remove adsorbed impurities, oven-dried at 70°C, and kept in a desiccator. For the sake of accuracy, the solubility product of our calcite substrate was verified by equilibrating a series of calcite suspensions in Milli-Q[®] water in centrifuge tubes under constant stirring for 10 days. After this time, pH, alkalinity, and the total calcium concentration (ΣCa, determined by AAS) were measured and the Ca²⁺ and CO₃²⁻

120 activities calculated with MINEQL+ v.4.6 software.³⁴ The measured $\log_{10} K_{sp}^o$ was -8.48 ± 0.04 , in excellent agreement with the value selected by the National Institute of Standards and Technology.^{32,60}

125 Verification of the experimental system and specific details of acidimetric and calcium titrations

To check for possible mass exchange (between the suspension and the atmosphere) during the course of our experiments, preliminary equilibration experiments (without titrant additions), using the re-equilibrated $\text{CaCO}_{3(s)}$ suspensions, were performed over extended periods of time (7-10 days) and their chemistry monitored using the three ISEs. In a perfectly closed $\text{CaCO}_{3(s)}\text{-H}_2\text{O}$ system at equilibrium, pH, pCa, and pCO_3 should remain constant and reproduce the calcite solubility product. Both criteria were met in these experiments. In addition, the performance of the ISEs was evaluated by examining the self-consistency of the ion activity product (IAP, $a_{\text{Ca}^{2+}} \times a_{\text{CO}_3^{2-}}$) in two preliminary acidimetric titrations performed between pH 9.5 and 7.5 at conditions identical to those of experiments TH-I, TH-III, TH-IV and TH-VI. Throughout both titrations, the Ca^{2+} and CO_3^{2-} activities measured after a minimum of three hours following titrant additions closely reproduced the solubility product of calcite ($\geq 95\%$) which confirmed the re-establishment of bulk equilibrium (Figure A1). Upon confirmation of the performance of the experimental system, acidimetric titrations were conducted by stepwise addition of varying volumes (0.3 to 1.2 mL) of standardized 0.1 M HCl solutions to pre-equilibrated calcite suspensions prepared at different initial chemical conditions (Table 2 in main text). The ISE measurements were recorded at least three hours after each titrant addition but longer time intervals (up to 12 hours) were also investigated to confirm full restoration of bulk equilibrium. Complete titrations required from 4 to 5 days. Similarly, calcium titrations were conducted by stepwise additions of varying volumes (0.05 to 2 mL) of a standardized 0.4 M CaCl_2 solution to pre-equilibrated calcite suspensions prepared at different initial chemical conditions (Table 2 in main text). The initial conditions for these titration were carefully chosen to allow for detectable changes in Ca^{2+} activities upon CaCl_2 addition and to expand the range of total calcium concentration (ΣCa) covered by each titration experiment. To this end, the initial composition of the suspensions was controlled by differential additions of HCl, KHCO_3 , and/or Na_2CO_3 solutions to set their respective initial pH, ΣCa , and ΣCO_2 before the *first equilibration* period (Table 2). Preliminary calcium titrations revealed that a period of at least 18 hours is necessary to obtain stable ISE readings after each discrete CaCl_2 addition. Hence, data for these experiments were acquired after at least 24 hours of equilibration following each CaCl_2 addition. Complete titrations required between 5 and 8 days.

Additional titrations were conducted using dilute calcite suspensions (0.4 g L^{-1} equivalent to $0.18 \text{ m}^2 \text{ L}^{-1}$) prepared in a 0.02 M KCl solution (Experiments TH-VI and TCa-IV, respectively) under conditions identical to at least one acidimetric and one calcium surface titration experiment. They served to: i) evaluate “mass effects” influencing sorption

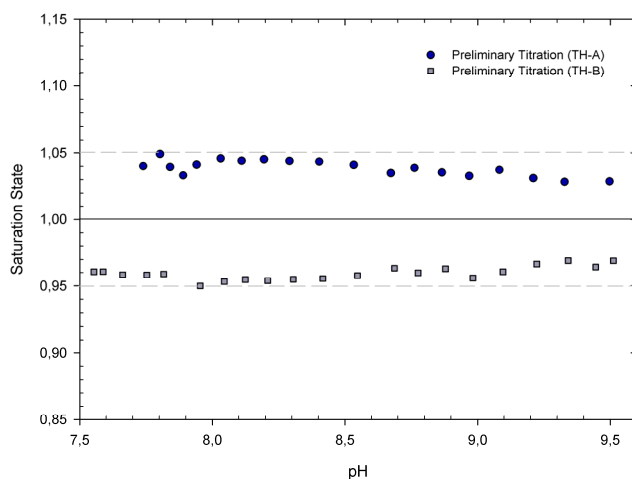


Fig. A1 Calcite saturation state computed from Ca^{2+} and CO_3^{2-} ISE measurements throughout two preliminary acidimetric titrations (solid:solution ratio of 9.61 g L^{-1}) to verify the performance of the ISEs electrodes and confirm achievement of bulk equilibrium conditions.

behavior by properly accounting for dissolution (acidimetric titrations) and precipitation (calcium titrations) while the surface available for adsorption reactions is low (i.e., bulk reactions dominate over surface interactions), and ii) detect possible “background effects” (e.g., adsorption) associated to the titration system. Since the bulk kinetics of dissolution and precipitation are proportional to the reactive surface area of the mineral, equilibration times for the “blank” runs were longer than for equivalent titrations performed at higher solid:solution ratios, and therefore, data were only recorded once stable ISEs readings were obtained (after ~ 7 hours for acidimetric and ~ 30 hours for calcium titrations). After each titration experiment, the ISEs were re-calibrated to verify their performance and evaluate the electrode drift. In all cases, electrode drift was $< 3\%$, and thus, considered acceptable. To prevent carry-over contamination from preceding experiments, the reaction vessel and its components were acid-washed (with 5% v/v HCl solutions) and rinsed with Milli-Q[®] water before each titration and the pH and pCa of the Milli-Q[®] water stored in the fully-assembled reaction vessel were monitored for several hours to confirm the absence of contaminants (i.e., H^+ , Ca^{2+}) possibly adhering to components of the reaction vessel. Low pH and relatively high ΣCO_2 conditions allowing for moderate to high carbonic acid concentrations in the experimental system were avoided to prevent the formation of $\text{CO}_{2(g)}$ nuclei inside the reaction vessel and ensure that the ΣCO_2 an proton mass conservation conditions required by our titration protocol were met (see main text). For instance, CO_2 bubble nucleation was observed in some titrations carried out to a pH of approximately 6.7. A judicious selection of initial pH, ΣCa , and ΣCO_2 conditions (Table 2 in main text) guaranteed that sufficiently low levels of carbonic acid were maintained throughout our titrations to prevent $\text{CO}_{2(g)}$ bubble formation while covering a pH range from 7.1 to 9.7. The maximum concentration of H_2CO_3 registered at the end of our experiments was $\sim 4 \cdot 10^{-4} \text{ M}$.

Correction of sorption data

As explained in the main text, to properly compute *net* sorption densities from titration experiments not initiated at the ZNSRC, the initial extent of proton occupancy of the pre-equilibrated calcite sample (subsequently subjected to acidimetric or calcium titrations) must be considered. By re-arranging equation 11 (with $n=1$) and using the initial pH and pCa values measured after the *second equilibration* period in each experiment initiated away from the ZNSRC, the respective initial occupancy ratios (*Ratio^{occ}*) can be calculated according to:

$$Ratio^{occ} = \left(\frac{(aH^+)^2 K_{Exc}}{aCa^{2+}} \right) = \left(\frac{X_{\equiv Ca(HCO_3)_2(exc)}^0}{X_{\equiv CaCO_3)_2(exc)}^0} \right) = \left(\frac{[\equiv Ca(HCO_3)_2(exc)]^0}{[\equiv CaCO_3)_2(exc)]^0} \right) \quad (I)$$

which is equally expressed in mole fractions or molar concentrations of “exchangeable lattice species” at the beginning of the experiment (identified with the superscript “0”). The total molar concentration of cation exchangeable sites, $[\equiv CaCO_3)_2(exc)]^{TOT}$, available in each experiment is obtained from:

$$[\equiv Ca(HCO_3)_2(exc)]^0 + [\equiv CaCO_3)_2(exc)]^0 = ECSD \cdot A \cdot S = [\equiv CaCO_3)_2(exc)]^{TOT} \quad (II)$$

Thus, the initial molar proton occupancy, $[\equiv Ca(HCO_3)_2(exc)]^0$, at the beginning of each experiment is given by:

$$[\equiv Ca(HCO_3)_2(exc)]^0 = \left(\frac{Ratio^{occ} \cdot [\equiv CaCO_3)_2(exc)]^{TOT}}{1 + Ratio^{occ}} \right) \quad (III)$$

Finally, the corrected adsorption data (moles L⁻¹), $[H]_{ads}^{corr}$, used in FITEQL optimizations are obtained with:

$$[H]_{ads}^{corr} = (\Gamma_H^{app} \cdot A \cdot S) + 2 [\equiv Ca(HCO_3)_2(exc)]^0 \quad (IV)$$

This correction was refined iteratively by averaging the K_{ex} and ECSD obtained from data sets of experiments TH-I, TH-III, TH-IV and TH-VI with those obtained with corrected adsorption data from experiments TH-II and TH-V. Using the average K_{ex} and ECSD values, sorption data of the latter experiments were re-adjusted (*Ratio^{occ}* and $[\equiv Ca(HCO_3)_2(exc)]^0$ were re-calculated) and K_{ex} and ECSD re-optimized as before. This procedure was performed until the estimated $[H^+]_{ads}^{corr}$ values and those calculated in the preceding optimization converged to within ± 0.5 %. (Note that Γ_H^{net} is obtained by dividing $[H]_{ads}^{corr}$ by $A \cdot S$). This correction applies to proton and calcium titration data because, as explained in the main text, net proton uptake was observed in both types of titration experiments.

Equilibrium speciation calculations involving ion exchange

Speciation calculations, including reaction 3 (see main text), were performed with an in-house Matlab[®] subroutine integrating the Newton-Raphson iterative method where, in contrast to MINEQL+ v4.6, the mass action law and mass balance matrices are decoupled to specify suitable stoichiometric coefficients (reaction 3) for the principal chemical components H⁺ and Ca²⁺. For illustrative purposes, the former, formulated in terms of the *tableau* method,³¹ is displayed in Table A-I. The Matlab[®] subroutines can be obtained upon request to the lead author.

The relevant mass balance equations specified in the code are as follows:

$$\Sigma H_{Het} = TOTH + 2 [\equiv Ca(HCO_3)_2(exc)] \quad (V)$$

$$\Sigma Ca_{Het} = TOTCa + [\equiv CaCO_3)_2(exc)] \quad (VI)$$

where ΣH_{Het} and ΣCa_{Het} are the calculated mass balances for proton and calcium involving the aqueous and the solid phase, TOTH and TOTCa are the quantities defined in Table 3 and the species in brackets are molar concentrations of the exchangeable cation species (solid phase). Provided all exchangeable cation sites remain unreacted and available for proton uptake, equations V and VI are subjected to the following constraints:

$$\Sigma H_{Theo} = TOTH = C_A - C_B \quad (VII)$$

= Total known excess or deficit of protons in the system

and,

$$\Sigma Ca_{Theo} = \Sigma Ca + [\equiv CaCO_3)_2(exc)]^{TOT} \quad (VIII)$$

= Total known excess or deficit of calcium in the system

The stoichiometric coefficients of principal components H⁺ and Ca²⁺ defining the formation of exchangeable species in the mass balance matrix are given by equations V and VI (i.e., 2 and 1 respectively) whereas those corresponding to the mass action law matrix are defined by the stoichiometry of reaction 3. As in all previous calculations with MINEQL+, the stoichiometric coefficients of all other chemical species (aqueous phase) remain identical in both the mass action law and mass balance matrices. This procedure allows to properly compute equilibrium speciation of a carbonate system involving reaction 3 as formulated in terms of the principal chemical component: $[\equiv CaCO_3)_2(exc)]$. If protons already occupy a fraction of the lattice exchangeable sites in the calcite powder, the ΣH_{Het} and the ΣCa_{Het} constraints must be modified to consider the amount of $[\equiv Ca(HCO_3)_2(exc)]$ already present (proton excess and calcium deficit) within the calcite specimen. For example, in the case of an originally pure, hydrogen-free, calcite specimen subsequently treated with a “pre-treatment” acid solution (acid leaching) and later subjected to different solution conditions, $[\equiv Ca(HCO_3)_2(exc)]^0$ and $[\equiv CaCO_3)_2(exc)]^0$ are first estimated from speciation calculations using the calibrated K_{ex} value, and the known chemical composition of the “pre-treatment” solution. These values are then used to modify the ΣH_{Theo} and the ΣCa_{Theo} constraints imposed to the equilibrium speciation problem (Eqs. VII and VIII, *via* the mass balance matrix) as follows:

$$\Sigma H_{Theo} = TOTH_{New} + 2 [\equiv Ca(HCO_3)_2(exc)]^0 \quad (IX)$$

$$\Sigma Ca_{Theo} = \Sigma Ca_{New} + [\equiv CaCO_3)_2(exc)]^0 \quad (X)$$

where $TOTH_{New}$ and ΣCa_{New} are known quantities and pertain to the experimental solution to which the calcite powder is subjected after “pre-treatment” (before calcite immersion in experimental solution) and $[\equiv CaCO_3)_2(exc)]^0 = [\equiv CaCO_3)_2(exc)]^{TOT} - [\equiv Ca(HCO_3)_2(exc)]$. Note that twice the value of $[\equiv Ca(HCO_3)_2(exc)]$ must be added to $TOTH_{New}$ to properly account for the excess in protons present in the system, whereas $[\equiv Ca(HCO_3)_2(exc)]$ must be subtracted from $[\equiv CaCO_3)_2(exc)]^{TOT}$ to account for the Ca²⁺ equivalents (removed during “pre-treatment”) that are no longer present in the new CaCO_{3(s)}-H₂O system.

TABLE A-I Tableau-based Formulation of Chemical Speciation Problem for the CaCO_{3(s)}-KCl-H₂O System (Mass Action Law Matrix)

Aqueous Phase Species	Principal Chemical Components						Log ₁₀ K° (25 °C)
	H ⁺	Ca ²⁺	K ⁺	Cl ⁻	CaCO _{3(s)}	≡(CaCO ₃) ₂ (exc)	
H ⁺	1						0
Ca ²⁺		1					0
K ⁺			1				0
Cl ⁻				1			0
CO ₃ ²⁻		-1			1		Log ₁₀ K° _{sp}
OH ⁻	-1						Log ₁₀ K° _w
HCO ₃ ⁻	1	-1			1		Log ₁₀ K° _{sp} + Log ₁₀ K° _{HCO3}
H ₂ CO ₃	2	-1			1		Log ₁₀ K° _{sp} + Log ₁₀ K° _{HCO3} + Log ₁₀ K° _{H2CO3}
CaOH ⁺	-1	1					Log ₁₀ K° _{CaOH}
CaCO ₃ (aq)					1		Log ₁₀ K° _{sp} + Log ₁₀ K° _{CaCO3}
CaHCO ₃ ⁺	1				1		Log ₁₀ K° _{sp} + Log ₁₀ K° _{CaHCO3} + Log ₁₀ K° _{HCO3}
CaCl ⁺		1		1			Log ₁₀ K° _{CaCl}
KCl			1	1			Log ₁₀ K° _{KCl}
Solid Phase Species							
(≡CaCO ₃) ₂ (exc)						1	0
≡Ca(HCO ₃) ₂ (exc)	2	-1				1	Log ₁₀ °K _{ex}
SUM (mol / L)	C _A - C _B	ΣCa	ΣK	ΣCl	ΣCO ₂	ECSD · S · A	

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(RAW DATA)

CaCO_{3(s)} Solubility Product Data

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Exp. ID	pH	ΣCa (mol L ⁻¹)	Alkalinity (mol L ⁻¹)	I (mol L ⁻¹)	Log ₁₀ K _{sp} ^o
K _{sp} -1	9.87	1.16·10 ⁻⁴	2.51·10 ⁻⁴	3.8·10 ⁻⁴	-8.49
K _{sp} -2	9.75	1.23·10 ⁻⁴	2.37·10 ⁻⁴	3.8·10 ⁻⁴	-8.52
K _{sp} -3	9.75	1.33·10 ⁻⁴	2.54·10 ⁻⁴	4.1·10 ⁻⁴	-8.45
K _{sp} -4	9.78	1.39·10 ⁻⁴	2.26·10 ⁻⁴	4.0·10 ⁻⁴	-8.49
K _{sp} -5	9.73	1.34·10 ⁻⁴	2.57·10 ⁻⁴	4.1·10 ⁻⁴	-8.45
K _{sp} -6	9.60	1.39·10 ⁻⁴	2.43·10 ⁻⁴	4.1·10 ⁻⁴	-8.52
K _{sp} -7	9.63	1.45·10 ⁻⁴	2.38·10 ⁻⁴	4.2·10 ⁻⁴	-8.50
K _{sp} -8	9.68	1.40·10 ⁻⁴	2.59·10 ⁻⁴	4.2·10 ⁻⁴	-8.45
K _{sp} -9	9.67	1.43·10 ⁻⁴	2.57·10 ⁻⁴	4.3·10 ⁻⁴	-8.45
K _{sp} -10	9.84	1.10·10 ⁻⁴	2.57·10 ⁻⁴	3.7·10 ⁻⁴	-8.50
K _{sp} -11	9.70	1.03·10 ⁻⁴	2.68·10 ⁻⁴	3.6·10 ⁻⁴	-8.54
K _{sp} -12	9.72	1.31·10 ⁻⁴	2.63·10 ⁻⁴	4.1·10 ⁻⁴	-8.45
K _{sp} -13	9.71	1.37·10 ⁻⁴	2.45·10 ⁻⁴	4.1·10 ⁻⁴	-8.47
K _{sp} -14	9.76	1.27·10 ⁻⁴	2.42·10 ⁻⁴	3.9·10 ⁻⁴	-8.49
K _{sp} -15	9.78	1.22·10 ⁻⁴	2.47·10 ⁻⁴	3.8·10 ⁻⁴	-8.49
K _{sp} -16	9.61	1.35·10 ⁻⁴	2.37·10 ⁻⁴	4.0·10 ⁻⁴	-8.53
K _{sp} -17	9.75	1.31·10 ⁻⁴	2.71·10 ⁻⁴	4.1·10 ⁻⁴	-8.42
K _{sp} -18	9.71	1.37·10 ⁻⁴	2.8·10 ⁻⁴	4.3·10 ⁻⁴	-8.40
K _{sp} -19	9.70	1.34·10 ⁻⁴	2.64e-4	4.2·10 ⁻⁴	-8.45
K _{sp} -20	9.70	1.31·10 ⁻⁴	2.41e-4	4.0·10 ⁻⁴	-8.50
					-8.48 ± 0.04

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Exp. ID	pH	pCa	Log ₁₀ [K ⁺]	Log ₁₀ [Cl ⁻]	TOTH* _{Theo} (mol L ⁻¹)	I ^a (mol L ⁻¹)	Exp. ID	pH	pCa	Log ₁₀ [K ⁺]	Log ₁₀ [Cl ⁻]	TOTH* _{Theo} (mol L ⁻¹)	I ^a (mol L ⁻¹)
TH-I							TH-II						
TH-I-1	9.27	3.70	-1.66	-1.66	2.35·10 ⁻⁴	0.023	TH-II-1	8.37	3.36	-1.66	-1.66	8.32·10 ⁻⁴	0.024
TH-I-2	9.15	3.66	-1.66	-1.66	3.10·10 ⁻⁴	0.023	TH-II-2	8.26	3.28	-1.66	-1.66	9.43·10 ⁻⁴	0.024
TH-I-3	9.04	3.54	-1.66	-1.65	3.85·10 ⁻⁴	0.023	TH-II-3	8.22	3.04	-1.66	-1.66	1.01·10 ⁻³	0.026
TH-I-4	8.82	3.46	-1.66	-1.65	4.59·10 ⁻⁴	0.023	TH-II-4	8.18	3.01	-1.66	-1.66	1.08·10 ⁻³	0.026
TH-I-5	8.70	3.37	-1.66	-1.65	5.84·10 ⁻⁴	0.024	TH-II-5	8.12	3.01	-1.66	-1.66	1.14·10 ⁻³	0.026
TH-I-6	8.54	3.32	-1.66	-1.65	7.08·10 ⁻⁴	0.024	TH-II-6	8.00	2.93	-1.66	-1.66	1.34·10 ⁻³	0.027
TH-I-7	8.48	3.27	-1.66	-1.65	8.56·10 ⁻⁴	0.024	TH-II-7	7.93	2.91	-1.66	-1.66	1.47·10 ⁻³	0.027
TH-I-8	8.41	3.16	-1.66	-1.65	9.30·10 ⁻⁴	0.024	TH-II-8	7.86	2.88	-1.66	-1.66	1.60·10 ⁻³	0.028
TH-I-9	8.28	3.11	-1.66	-1.65	1.00·10 ⁻³	0.025	TH-II-9	7.81	2.82	-1.66	-1.66	1.73·10 ⁻³	0.028
TH-I-10	8.11	3.06	-1.66	-1.64	1.15·10 ⁻³	0.025	TH-II-10	7.74	2.81	-1.66	-1.66	1.86·10 ⁻³	0.029
TH-I-11	8.05	3.00	-1.66	-1.64	1.40·10 ⁻³	0.025	TH-II-11	7.70	2.81	-1.66	-1.66	2.00·10 ⁻³	0.029
TH-I-12	7.99	2.95	-1.66	-1.64	1.52·10 ⁻³	0.026	TH-II-12	7.63	2.80	-1.66	-1.66	2.13·10 ⁻³	0.029
TH-I-13	7.91	2.93	-1.66	-1.64	1.64·10 ⁻³	0.026	TH-II-13	7.60	2.77	-1.66	-1.66	2.34·10 ⁻³	0.030
TH-I-14	7.88	2.88	-1.66	-1.64	1.76·10 ⁻³	0.027	TH-II-14	7.54	2.72	-1.66	-1.66	2.56·10 ⁻³	0.031
TH-I-15	7.79	2.85	-1.66	-1.63	1.89·10 ⁻³	0.027	TH-II-15	7.47	2.73	-1.66	-1.66	2.77·10 ⁻³	0.031
							TH-II-16	7.43	2.70	-1.66	-1.66	2.99·10 ⁻³	0.031
							TH-II-17	7.38	2.68	-1.66	-1.66	3.20·10 ⁻³	0.032
							TH-II-18	7.34	2.67	-1.66	-1.66	3.41·10 ⁻³	0.032
TH-III							TH-IV						
TH-III-1	9.45	3.57	-1.66	-1.65	1.58·10 ⁻⁴	0.023	TH-IV-1	9.51	3.62	-1.66	-1.65	1.23·10 ⁻⁴	0.023
TH-III-2	9.31	3.63	-1.66	-1.65	2.25·10 ⁻⁴	0.023	TH-IV-2	9.34	3.51	-1.66	-1.65	1.85·10 ⁻⁴	0.023
TH-III-3	9.18	3.55	-1.66	-1.65	2.91·10 ⁻⁴	0.023	TH-IV-3	9.22	3.42	-1.66	-1.65	2.48·10 ⁻⁴	0.023
TH-III-4	9.06	3.52	-1.66	-1.65	3.58·10 ⁻⁴	0.023	TH-IV-4	9.10	3.38	-1.66	-1.65	3.10·10 ⁻⁴	0.023
TH-III-5	8.95	3.46	-1.66	-1.65	4.24·10 ⁻⁴	0.023	TH-IV-5	8.98	3.35	-1.66	-1.65	3.72·10 ⁻⁴	0.023
TH-III-6	8.85	3.37	-1.66	-1.65	4.90·10 ⁻⁴	0.024	TH-IV-6	8.88	3.31	-1.66	-1.65	4.35·10 ⁻⁴	0.024
TH-III-7	8.76	3.41	-1.66	-1.65	5.56·10 ⁻⁴	0.024	TH-IV-7	8.78	3.29	-1.66	-1.65	4.97·10 ⁻⁴	0.024
TH-III-8	8.59	3.28	-1.66	-1.65	6.88·10 ⁻⁴	0.024	TH-IV-8	8.69	3.21	-1.66	-1.65	5.59·10 ⁻⁴	0.024
TH-III-9	8.45	3.19	-1.66	-1.64	8.20·10 ⁻⁴	0.025	TH-IV-9	8.55	3.17	-1.66	-1.64	6.83·10 ⁻⁴	0.025
TH-III-10	8.33	3.12	-1.66	-1.64	9.51·10 ⁻⁴	0.025	TH-IV-10	8.42	3.12	-1.66	-1.64	8.06·10 ⁻⁴	0.025
TH-III-11	8.23	3.09	-1.66	-1.64	1.08·10 ⁻³	0.026	TH-IV-11	8.30	3.08	-1.66	-1.64	9.30·10 ⁻⁴	0.026
TH-III-12	8.09	3.02	-1.66	-1.64	1.30·10 ⁻³	0.026	TH-IV-12	8.21	3.04	-1.66	-1.64	1.05·10 ⁻³	0.026
TH-III-13	7.97	2.89	-1.66	-1.63	1.52·10 ⁻³	0.028	TH-IV-13	8.12	3.00	-1.66	-1.64	1.18·10 ⁻³	0.028
TH-III-14	7.86	2.86	-1.66	-1.63	1.73·10 ⁻³	0.028	TH-IV-14	8.05	2.99	-1.66	-1.64	1.30·10 ⁻³	0.028
TH-III-15	7.79	2.88	-1.66	-1.63	1.95·10 ⁻³	0.028	TH-IV-15	7.85	2.89	-1.66	-1.63	1.66·10 ⁻³	0.028
							TH-IV-16	7.75	2.87	-1.66	-1.63	1.91·10 ⁻³	0.028
							TH-IV-17	7.66	2.84	-1.66	-1.62	2.15·10 ⁻³	0.028
							TH-IV-18	7.59	2.80	-1.66	-1.62	2.39·10 ⁻³	0.028
TH-V							TH-VI						
TH5-V-1	7.67	2.73	-1.66	-1.58	1.14·10 ⁻³	0.032	TH-VI-1	9.33	3.77	-1.66	-1.65	1.99·10 ⁻⁴	0.023
TH5-V-2	7.62	2.72	-1.66	-1.58	1.35·10 ⁻³	0.032	TH-VI-2	9.10	3.70	-1.66	-1.65	3.12·10 ⁻⁴	0.023
TH5-V-3	7.54	2.69	-1.66	-1.57	1.57·10 ⁻³	0.033	TH-VI-3	9.03	3.64	-1.66	-1.65	3.27·10 ⁻⁴	0.023
TH5-V-4	7.49	2.68	-1.66	-1.57	1.78·10 ⁻³	0.033	TH-VI-4	8.85	3.59	-1.66	-1.65	4.48·10 ⁻⁴	0.023
TH5-V-5	7.44	2.65	-1.66	-1.57	1.99·10 ⁻³	0.034	TH-VI-5	8.77	3.54	-1.66	-1.65	4.95·10 ⁻⁴	0.023
TH5-V-6	7.38	2.64	-1.66	-1.57	2.20·10 ⁻³	0.034	TH-VI-6	8.61	3.50	-1.66	-1.65	6.44·10 ⁻⁴	0.024
TH5-V-7	7.34	2.62	-1.66	-1.56	2.41·10 ⁻³	0.035	TH-VI-7	8.52	3.46	-1.66	-1.65	7.34·10 ⁻⁴	0.024
TH5-V-8	7.32	2.62	-1.66	-1.56	2.62·10 ⁻³	0.035	TH-VI-8	8.40	3.39	-1.66	-1.64	8.41·10 ⁻⁴	0.024
TH5-V-9	7.26	2.61	-1.66	-1.56	2.82·10 ⁻³	0.035	TH-VI-9	8.23	3.33	-1.66	-1.64	1.08·10 ⁻³	0.024
TH5-V-10	7.27	2.65	-1.66	-1.56	2.93·10 ⁻³	0.035	TH-VI-10	8.17	3.28	-1.66	-1.64	1.12·10 ⁻³	0.025
							TH-VI-11	8.07	3.23	-1.66	-1.64	1.29·10 ⁻³	0.025
							TH-VI-12	8.01	3.19	-1.66	-1.64	1.34·10 ⁻³	0.025
							TH-VI-13	7.95	3.17	-1.66	-1.63	1.47·10 ⁻³	0.026

^a Ionic strength calculated iteratively using the experimental pH and pCa measurements

CaCl₂ Titrations Data

Exp. ID	pH	pCa	Log ₁₀ [K ⁺]	Log ₁₀ [Cl ⁻]	TOTCa ⁺ _{Theo} (mol L ⁻³)	I ^a (mol L ⁻¹)	Exp. ID	pH	pCa	Log ₁₀ [K ⁺]	Log ₁₀ [Cl ⁻]	TOTCa ⁺ _{Theo} (mol L ⁻³)	I ^a (mol L ⁻¹)
TCa-I							TCa-II						
TCa-I-1	9.04	4.60	-1.67	-1.82	-5.74·10 ⁻³	0.020	TCa-II-1	9.06	4.72	-1.63	-1.92	-1.08·10 ⁻²	0.024
TCa-I-2	8.96	4.55	-1.67	-1.81	-5.61·10 ⁻³	0.020	TCa-II-2	8.91	4.57	-1.63	-1.91	-1.07·10 ⁻²	0.024
TCa-I-3	8.55	4.17	-1.67	-1.80	-5.42·10 ⁻³	0.021	TCa-II-3	8.78	4.38	-1.63	-1.90	-1.06·10 ⁻²	0.024
TCa-I-4	8.22	3.86	-1.67	-1.79	-5.17·10 ⁻³	0.021	TCa-II-4	8.64	4.17	-1.63	-1.89	-1.03·10 ⁻²	0.024
TCa-I-5	7.48	3.10	-1.67	-1.71	-3.59·10 ⁻³	0.025	TCa-II-5	8.26	3.87	-1.63	-1.86	-9.85·10 ⁻³	0.024
TCa-I-6	7.22	2.83	-1.67	-1.65	-2.03·10 ⁻³	0.029	TCa-II-6	7.95	3.62	-1.63	-1.83	-9.38·10 ⁻³	0.024
TCa-I-7	7.16	2.74	-1.67	-1.62	-1.26·10 ⁻³	0.031	TCa-II-7	7.57	3.19	-1.63	-1.78	-8.44·10 ⁻³	0.026
TCa-III							TCa-IV						
TCa-III-1	8.40	4.73	-1.67	-2.90	-2.22·10 ⁻²	0.023	TCa-IV-1	9.19	4.50	-1.67	-1.82	-5.74·10 ⁻³	0.027
TCa-III-2	7.83	4.10	-1.67	-2.50	-2.12·10 ⁻²	0.023	TCa-IV-2	8.98	4.35	-1.67	-1.82	-5.55·10 ⁻³	0.028
TCa-III-3	7.70	3.94	-1.67	-2.42	-2.09·10 ⁻²	0.023	TCa-IV-3	8.68	3.85	-1.67	-1.82	-5.42·10 ⁻³	0.028
TCa-III-4	7.55	3.44	-1.67	-2.36	-2.06·10 ⁻²	0.023	TCa-IV-4	8.39	3.71	-1.67	-1.82	-5.17·10 ⁻³	0.029
							TCa-IV-5	7.49	3.07	-1.67	-1.79	-3.60·10 ⁻³	0.032

^a Ionic strength calculated iteratively using the experimental pH and pCa measurements

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