The presence of adsorbed ions on calcite surfaces can significantly affect the adsorption and desorption of organic molecules, which is critical for oil recovery and biomineralization. In this study, the structure of calcite–artificial seawater interfaces from 25 to 80 °C was experimentally and theoretically investigated by surface X-ray scattering and molecular dynamics simulations, respectively. The small difference in the CTR scattering profiles at different temperatures could be attributed to the relaxed outermost calcite surface. The electron density profile of the NaCl solution (0.5 mol/kg) exhibits peaks near the calcite surfaces. The two peaks closest to the surface can be interpreted as adsorbed water molecules, inner–sphere Na⁺ complexes, and inner– and outer–sphere Cl⁻ complexes. Thus, the adsorbed Cl⁻ formed two peaks near the calcite’s surface, while Na⁺ formed a single peak as an inner–sphere complex. It should be noted that there was no strong covalent bond between these inner–sphere complexes and the calcite surface. These structural differences between adsorbed cations and anions could be explained by the balance of the interactions between the surface Ca²⁺ and CO₃²⁻, adsorbed ions, and the surrounding water molecules. The presence of inner–sphere Cl⁻ complexes destabilizes surface Ca²⁺, whereas Na⁺ has an insignificant effect on the structure of surface CO₃²⁻. Adding a small amount (0.045 mol/kg) of Mg²⁺ and SO₄²⁻ appears to enhance the relaxation of the interfacial structure.

**Keywords**: Calcite, Water, Interface, Surface X-ray scattering, Molecular dynamics

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**INTRODUCTION**

Carbonate minerals are ubiquitous in both natural environments and industrial materials. The sorption and release of foreign ions at carbonate–mineral surfaces are critical for the growth and dissolution of crystals (Reddy and Nancollas, 1976; Meyer, 1984; Davis et al., 2000; Wasyleñki et al., 2005a, 2005b; Lin and Singer, 2009; Lopez et al., 2009; Bracco et al., 2012; Nielsen et al., 2013), recovery of various ions from the environment (Fulghum et al., 1988; Tesoriero and Pankow, 1996; Reeder et al., 1999; Godelitsas et al., 2003; Callagon et al., 2014; Andersson et al., 2014, 2016.), estimation of past temperatures (Morse et al., 1997, 2007; Lopez et al., 2009), and altering wettability leading to enhanced oil recovery (Zhang et al., 2006, 2007; Strand et al., 2008; Sakuma et al., 2014; Mohammed and Babadagli, 2015).

Calcite, which is the major component of carbonate rocks, has a cleavage plane {10.4}, and natural mineral crystal surfaces are also {10.4} faces. Therefore, the interface between calcite and aqueous solutions is of primary importance in natural environments. Electrolytes in water influence the solubility of calcite; its dissolution rate is enhanced with increasing salt concentrations (Ruiz–Agudo et al., 2009, 2010). The adsorption and incorporation of Mg²⁺ and SO₄²⁻ onto a calcite surface has a major impact on the wettability of calcite (Reddy and Nancollas, 1976; Meyer, 1984; Davis et al., 2000; De Leeuw, 2002; De Leeuw et al., 2002; Wasyleñki et al.,...
The structure of adsorbed ions and water molecules provide much information about the roles that the ions play in the physicochemical properties of calcite surfaces, therefore, these structures have been studied using molecular simulations and experiments. Molecular dynamics (MD) simulations of calcite–salt water interfaces have been conducted at an elevated temperature of 377 K, pressure of 24.1 MPa, and Cl⁻ concentrations of 1.86 and 3.7 mol/L (Chen et al., 2015). Inner–sphere Na⁺ and Cl⁻ complexes have been observed at the calcite {10.4} surface (Chen et al., 2015). These structures may differ from those in natural environments, such as those at ambient conditions in seawater, where the salt concentration is approximately 0.6 mol/kg. Atomic force microscopy (AFM) and MD studies of the structure of a dilute NaCl solution (~ 0.1 mol/L) on a calcite surface (Ricci et al., 2013) proposed that Na⁺ can move closer to the surface than Cl⁻, however, inner–sphere complexes of these ions were not reported. The conclusion of the difference in the adsorption structure of Na⁺ and Cl⁻ in those studies (Ricci et al., 2013; Chen et al., 2015) is controversial, and it is unclear whether the difference is due to differences in temperature, pressure, and salt concentrations. Surface X-ray scattering is a powerful tool for determining the structure of these interfaces with a high spatial resolution, <1 Å. Most previous experiments have analyzed salt concentrations below 0.1 M, which are below the general salt concentration of seawater (Chiarello and Sturchio, 1995; Sturchio et al., 1997; Cheng et al., 1998; Fenter et al., 2000; Geissbühler et al., 2004; Heberling et al., 2011; Fenter and Sturchio, 2012; Fenter et al., 2013; Heberling et al., 2014; Callagon et al., 2014; Hofmann et al., 2016).

In this study, the interfacial structure of the calcite {10.4}–artificial seawater interface with an ionic strength of 0.5 mol/kg is investigated from 25 to 80 °C by X-ray crystal truncation rod (CTR) scattering and MD simulations. The obtained electron density profiles from the CTR are compared to those obtained from the MD simulations. The effect of electrolytes on the stability of the calcite surface is discussed considering the atomistic structures of adsorbed ions, water molecules, and surface ions.

### Experimental and Computational Details

#### Materials

A calcite powder (> 99.5%, 2 g; Wako Pure Chemical Industries, Ltd.) was mixed with ultrapure water (>18.2 MΩ cm, 200 mL) in air and stirred by a magnetic stirrer at 500 rpm for three days. This saturated calcite solution was passed through a filter paper (8 µm pore size) to remove any undissolved calcite powder from the solution. Two salt solutions were prepared as detailed in Table 1. Pure NaCl (99.95%) and MgSO₄·7H₂O (99.9%) powders were used to prepare these solutions. The ionic strengths of these solutions were fixed at 0.5 mol/kg, and the pH levels of solutions 1 and 2 were 7.8 and 7.7, respectively. The densities of these solutions were measured at a temperature range of 20–80 °C (Fig. S1; available online from https://doi.org/10.2465/jmps.180329) using a density meter (Anton Paar DMA 4500 M). These densities were used to estimate the X-ray absorption.

A single calcite crystal was cleaved by a razor with a surface area of 6 × 6 mm² and thickness of 1 mm. These calcite crystals were immediately (<30 sec) immersed in a calcite–saturated aqueous solution to avoid contamination. The lattice constants of the rhombohedral calcite were a = 4.9873 Å and c = 17.04941 Å in the hexagonal setting, as determined by powder X-ray diffraction analysis.

#### X-ray Crystal Truncation Rod (CTR) Measurements

A high-temperature cell was developed for controlling the temperature of mineral–liquid interfaces, and a schematic of this system is presented in Figure 1. The cell was composed of polychlorotrifluoroethylene (PCTFE). A single calcite crystal is placed at the center of the top of the cell. Salt solution in a bottle was degassed in a vacuum for 15 min. The sample cell was assembled in the solution to avoid trapping any air. The calcite–solution interface was covered with a polyimide film (thickness of 7.5 µm) to keep the calcite crystal in place and prevent the evaporation of water. The CTR signals are sensitive to the structure of the calcite surface, and we found that the intensity varied during the crystal growth. To reach the equilibrium at a high temperature, the sample cell was stored at the desired temperature for a few hours before measurement. The CTR signals were stabilized by this method, and we believe that crystal growth had no effect when the CTR measurements were taken. The sample cell was mounted on the diffractometer and surrounded by a rubber heater to control the temperature. The temperature of the

<table>
<thead>
<tr>
<th>Table 1. Concentrations of dissolved ions in calcite-saturated water</th>
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<tbody>
<tr>
<td><strong>Solution 1</strong> (SnCl)</td>
</tr>
<tr>
<td>Na⁺</td>
</tr>
<tr>
<td>Cl⁻</td>
</tr>
<tr>
<td>Mg²⁺</td>
</tr>
<tr>
<td>SO₄²⁻</td>
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</table>
sample was monitored by a thermocouple placed just below the calcite sample in the center of the cell. The surface temperature was monitored using a non-contact thermometer, which exhibited a temperature gradient of 2 °C between the surface and the bottom of the calcite sample. To prevent significant degassing during the experiments, the highest measurement temperature was 80 °C. The CTR measurements for the calcite/solution 1 interfaces were taken more than three times at room temperature and more than two times at elevated temperatures. The measurements for calcite/solution 2 interfaces were taken three times at room temperature and four times at 80 °C. Measurements were taken once at 45 and 61 °C, because there was no significant change as a function of temperature for these interfaces. The reproducibility of these measurements was confirmed.

X-ray CTR measurements were conducted at the BL-4C of the Photon Factory in the High-Energy Accelerator Research Organization (KEK-PF). Monochromatic X-rays at 11.0 keV were used for measurements. Spectral CTR scattering from the interface was measured to obtain the electron density perpendicular to the surface. The CTR scattering was obtained in the range of momentum transfer (Q) 0.25–6.13 Å⁻¹ using a silicon drift detector. Each scattered X-ray intensity was obtained using a rocking scan at a given Q value.

Analysis of X-ray CTR profiles

The measured X-ray CTR scattering intensities were corrected by considering the Lorentz factor, polarization factor, transmission factor, rod interception (Vlieg, 1997), and surface area. The electron density profiles of the calcite–aqueous solution interfaces were obtained using the Fourier transform of the best structural model fitted to the experimental CTR profiles. The structure factor of model F consists of a fixed semi-infinite bulk calcite structure $F_{\text{bulk}}$, a relaxed surface structure $F_{\text{surf}}$, and the structure of the outermost surface and liquid $F_{\text{interface-liquid}}$ as follows.

$$ F = F_{\text{bulk}} + F_{\text{surf}} + F_{\text{interface-liquid}} $$ (1).

The semi-infinite structure factor $F_{\text{bulk}}$ is calculated by summing the structure factors of a single bulk unit cell $F_{\text{bulk}}$ from the top layer to $-\infty$ (Vlieg, 2000). The relaxed surface structure was only optimized in the direction normal to the surface. Four CaCO₃ layers were included in the relaxed surface structure. To reduce the number of degrees of freedom of the fit, the following relationship was applied to C-O bonds by considering the tilting of the CO₃ group:

$$ \delta(C)(i) = \frac{\delta(O)_{\text{low}}(i) + \delta(O)_{\text{high}}(i)}{2} $$ (2),

where $\delta(O)_{\text{low}}(i)$ and $\delta(O)_{\text{high}}(i)$ are the displacements of O at low and high CO₃ group positions in the i-th layer, respectively, and $\delta(C)(i)$ is the displacement of C in the i-th layer.

The electron density of the interface and liquid, along with position z perpendicular to the surface, was expressed by the superposition of Gaussian distributions, which were applied for the solid–liquid (Fenter, 2002) and liquid–vapor (Magnussen et al., 1995) interfaces as follows.

$$ \rho_{\text{interface-liquid}}(z) = \rho_{\infty} \left( \sum_{n=1}^{11} \frac{a_n}{\sqrt{2\pi} \sigma_n} e^{-\frac{(z-d_n)^2}{2\sigma_n^2}} + \sum_{m=1}^{\infty} \frac{d}{\sqrt{2\pi} \sigma_m} e^{-\frac{(z-md)^2}{2\sigma_m^2}} \right) $$ (3),

where the first term in the parenthesis of the equation describes the density oscillation of the outermost calcite surface and liquid, and the second term describes the density of the bulk liquid. The first term can express the electron density without any constraint on the positions of Gaussian distributions, while the second term constrains the interval of the Gaussian distribution with a constant of $d$ (≈ 3.0 Å), which is useful for describing the semi-infinite liquid structure. The $a_n$, $\sigma_n$, $d_n$, and $\rho_{\infty}$ parameters were used to determine the intensity, width, and position of the Gaussian distribution functions, respectively. Additionally, $\rho_{\infty}$ is the electron density of the bulk liquid. The parameters of the width ($\sigma_n$) and positions ($m$) in the second term were determined to smoothly connect the first and second terms, as follows:
\[ \sigma_m = \sqrt{\sigma_0^2 + m^2} \]  \hspace{1cm} (4),
\[ \sigma_0^2 = 11\sigma_{10}^2 - 10\sigma_{11}^2 \]  \hspace{1cm} (5),
\[ \sigma^2 = \sigma_{11}^2 - \sigma_{10}^2 \]  \hspace{1cm} (6),

and
\[ l = \frac{d_{11}}{d} + 1 \]  \hspace{1cm} (7),

where the first term in Eq. 7 indicates the integer division. To reduce the number of fitting parameters, \( a_n \) for \( n = 6-11 \), and \( d_n \) and \( \sigma_n \) for \( n = 7-11 \) were fixed for all models as listed in Table S3 (available online from https://doi.org/10.2465/jmps.180329).

The structure factor \( F_{\text{interface+liquid}}(Q) \) is the Fourier transformation of Eq. 3 and is described as follows.
\[ F_{\text{interface+liquid}}(Q) = \rho_0 \left( \sum_{n=11}^{1} a_n e^{iQd_n} e^{-0.5\sigma_n^2 Q^2} + d \sum_{m=1}^{10} e^{iQmd} e^{-0.5\sigma_m^2 Q^2} \right) \]  \hspace{1cm} (8),

where the second term in the parenthesis is the summation of geometric progression, therefore, the summation can be obtained analytically.

Fitting analysis was conducted using a modified version of the ANA-ROD program (Vlieg, 2000) to include the liquid density structure. The results of the best-fit models were evaluated according to the goodness of fit values, \( \chi^2 \), and the residual, \( R \). These values were calculated as follows:
\[ \chi^2 = \frac{1}{n} \sum_{j=1}^{n} \left( \frac{|F_j|_{\text{model}} - |F_j|_{\text{exp}}}{\sigma_j} \right)^2 \]  \hspace{1cm} (9),
and
\[ R = \frac{\sum_{j=1}^{n}(|F_j|_{\text{exp}} - |F_j|_{\text{model}})}{\sum_{j=1}^{n}|F_j|_{\text{exp}}} \]  \hspace{1cm} (10),

where \( n \) is the number of data points, and \( \sigma_j \) and \( F_j \) are the statistical uncertainty (Bevington and Robinson, 2003) and structure factor of the \( j \)-th data point, respectively. The ‘model’ and ‘exp’ subscripts indicate the model and experimental structure factors, respectively.

The experimental CTR profiles were obtained in the limited range of the \( Q \) space limiting the spatial resolution. The electron density spatial resolution is estimated from \( L = 2\pi/Q_{\text{max}} \), where \( Q_{\text{max}} \) is the highest \( Q \) value in the experimental data. In this study, the resolution was approximately 1.0 Å. A broadening procedure (Fenter, 2002) of the electron density was conducted to consider the limited range of the \( Q \) value.

**Classical Molecular Dynamics Simulations**

Classical molecular dynamics (MD) simulations were conducted to elucidate the molecular structure of the calcite–NaCl solution interface. The interatomic potential energy is composed of two- and three-body terms that were tested for various minerals and water (Kawano et al., 2009b, 2009a; Miyake et al., 2010; Sakuma and Kawamura, 2011; Sakuma et al., 2013; Sakuma and Ichiki, 2016b). An advantage of this potential model is that the reproducibility of calcite structures is higher than that of previously proposed models, as discussed in the Supplementary Items (SI).

The two-body term of the potential energy \( U_{ij} \) acting between the \( i \)-th and \( j \)-th atoms is expressed by the Coulomb, short-range repulsion, van der Waals, and three covalent functions as follows:
\[ U_{ij}(r_{ij}) = \frac{1}{4\pi\varepsilon_0} \frac{ze_i z_j e^2}{r_{ij}} + f_0(b_i + b_j) \exp \left( \frac{a_i + a_j - r_{ij}}{b_i + b_j} \right) \]
\[ - \frac{\sigma_{ij}}{r_{ij}^6} + D_{1ij} \exp \left( -\beta_{1ij} r_{ij} \right) \]
\[ + D_{2ij} \exp \left( -\beta_{2ij} r_{ij} \right) + D_{3ij} \exp \left( -\beta_{3ij} (r_{ij} - r_{3ij})^2 \right) \]  \hspace{1cm} (11),

where \( r \) is the distance between the atoms, \( z \) is the partial charge, \( e \) is the charge of the electron, \( \varepsilon_0 \) is the permittivity of the vacuum, \( f_0 = 41.865 \text{ KJ nm}^{-3} \text{mol}^{-1} \) is a constant, \( a \) is the repulsion radius, \( b \) is the softness parameter, and \( c \) is the van der Waals coefficient. Parameters \( D_{1}, D_{2}, \beta_{1}, \) and \( \beta_{2} \) are used to describe the potential curve of the covalent bonds. The final Gaussian function is used to separate the intra- and interatomic potential functions.

The three-body terms acting between the \( i, j, \) and \( k \) atoms are expressed as follows:
\[ U_{ijk}(\theta_{ijk}, r_{ij}, r_{ik}) = -f \left[ \cos(z(\theta_{ijk} - \theta_0)) - 1 \right] (k_1 k_2)^{1/2} \]  \hspace{1cm} (12a),
\[ k_1 = \frac{1}{\exp[\beta r_{ijk} r_{3ij} - 1]} + 1 \]  \hspace{1cm} (12b),

and
where θ is the angle between the atoms, f is a parameter for energy conversion, θ₀ is a parameter for controlling the angle, and gₓ and rₓ are the parameters for controlling the critical distance to apply the three-body term.

The potential parameters of calcite, water, and NaCl are listed in Table S1 (available online from https://doi.org/10.2465/jmps.180329). The potential parameters of NaCl have been reported previously (Sakuma and Ichiki, 2016a, 2016b), while those of water for various mineral interfaces (Suzuki and Kawamura, 2004; Nakano and Kawamura, 2006; Sakuma and Kawamura, 2009, 2011; Sakuma et al., 2011; Itoh and Sakuma, 2015; Ishikawa et al., 2016) were slightly modified to prevent the dissociation of H₂O at elevated temperatures at the calcite surface. Such a reaction cannot be described in this force field. No significant differences were found between the structure and dynamics of water in the liquid phase here and those of the previous H₂O model. The parameters of calcite were determined by reproducing the lattice constants, structure, and atomic coordinates from ambient to elevated temperatures, as plotted in Figures S2, S3, and S4 (available online from https://doi.org/10.2465/jmps.180329). The interactions between ions and water molecules were tested by calculating the solvation enthalpies of ions in water. Those of NaCl and CaCl₂ in water were consistent with the experimental values, as listed in Table S2 (available online from https://doi.org/10.2465/jmps.180329). A detailed discussion concerning the reproducibility is available in the SI.

MD simulations of calcite–NaCl solution interfaces were conducted in the periodic unit cell, as shown in Figure 2. The solubility of calcite in the NaCl solution is low (5–15 mmol/kg H₂O) within this temperature range (Miller, 1952), therefore, the Ca²⁺ and CO₃²⁻ in the solution were neglected in this simulation. Canonical ensemble simulations were conducted by fixing the number of atoms, volume, and temperature, which was controlled by an every-step scaling method as an approximation of the Gaussian thermostat (Morishita, 2003). No significant difference was observed when using the Nosé–Hoover chain thermostat (Martyna et al., 1992). The size of the unit cell is listed in Table 2. To remove periodic boundary condition artifacts from the normal direction to the {104} calcite surface, Ewald correction (Yeh and Berkowitz, 1999) was employed along the z-direction. A salt concentration of 0.5 mol/L was reproduced by adding 13 Na⁺ and Cl⁻, and 1443 H₂O molecules to the simulation unit cell. The equation of motion was integrated using the velocity Verlet algorithm with a time step of 0.1 fs. MD simulations of 100 ps were conducted to reach the equilibrium, and subsequent simulations of 10 ns were used to obtain the density profiles of the interfaces. MD simulations were performed using an in-house program based on the MXDTRICL and MXDORTO (Sakuma and Kawamura, 2009) codes.

The pair correlation function between atoms was calculated using the following equation.

\[
P_{ij}(R) = \frac{\Delta R}{4\pi R^2} n_i(R) \sum_{i' = 1}^{N_h} \theta_i(0) \theta_i(t)\]

(13),

where \( R \) is the distance between atom \( i \) and \( j \), \( \Delta R \) is the resolution of the distance, and \( n_i \) is the number of atom pairs at distance \( R - \Delta R/2 < R < R + \Delta R/2 \).

The residence time of water molecules in the first hydration shell of ions was calculated using the time correlation function (Impey et al., 1983; Koneshan et al., 1998) defined by

\[
R(t) = \frac{1}{N_h} \sum_{i = 1}^{N_h} \Theta_i(0) \Theta_i(t)\]

(14),

where \( N_h \) is the hydration number in the first hydration shell, and \( \Theta_i(t) \) is the unit step function, which is one if a water molecule is in the first hydration shell at time \( t \) or otherwise, it is zero. The hydration number was calculated by counting the number of water molecules in the first minimum of the PCF. To remove the effect of the temporary excursion of a water molecule from the hydration...
shell, as conducted in previous works (Koneshan et al., 1998; Sakuma and Kawamura, 2011), the residence time $\tau$ was obtained by fitting a single exponential decay $A \exp(-t/\tau)$ to the $R(t)$ with a time range of 3 to 10 ps, where $A$ and $\tau$ are fitting parameters.

**RESULTS**

**X-ray CTR scattering profiles of calcite–NaCl solution interface**

The experimental X-ray CTR scattering profiles of the calcite–$\text{NaCl}$ interfaces are plotted in Figure 3a. The peak intensities at $Q \approx 2.1$, 4.15, and 6.2 Å$^{-1}$ correspond to the Bragg reflections 10.4, 20.8, and 30.12, respectively. The scattering profiles between the Bragg peaks reflect scattering from the calcite–$\text{NaCl}$ interface. The CTRs exhibit a clear trend with the increasing temperature from 25 up to 80 °C, when a decrease in intensity between the Bragg peaks is observed at $Q \approx 5.3$ to 5.6 Å$^{-1}$, and a small difference at 80 °C was observed at $Q \approx 3.2$ Å$^{-1}$.

**RESULTS**

**X-ray CTR scattering profiles of calcite–NaCl and calcite–NaCl+MgSO$_4$ interfaces**

The CTR profiles of the structural models that provide the best fit to the experimental data are shown as solid lines in Figure 3. The quality of the fits is determined by the $\chi^2$ values and R-factors, as listed in Table 3. The obtained electron density profiles of calcite–$\text{NaCl}$ are shown in Figure 4a, where the outermost calcite surface can be interpreted as $z = 0$ Å. The electron density profile of the CaCO$_3$ layers is characterized by two small peaks and one large peak corresponding to the two O layers and one CaCO layer, respectively, as shown in Figure 4a. The peak intensity at $z = 0$ Å for all temperatures was significantly lower than the peaks of the inner CaCO$_3$ layers at $z = -3$, $-6$, and $-9$ Å. The small changes in the peak positions of two O layers relative to the central CaCO layer were gradually relaxed by approaching from the surface to the bulk, and the peaks at $z = -11$ and $-13$ Å were similar to those of the peaks in the bulk. The two electron density maxima were observed at $z = 3.2$ and 6–8 Å in the liquid. The peak intensity in the liquid decreased with increasing temperature.

The obtained calcite–$\text{NaCl}+\text{MgSO}_4$ electron density profiles are shown in Figure 4b. The shapes of the electron densities were similar to those of the calcite–$\text{NaCl}$ interfaces, but the dependence of temperature was negligible at the calcite–$\text{NaCl}+\text{MgSO}_4$ interfaces.

**Electron density profiles of calcite–$\text{NaCl}$ calculated using molecular dynamics simulations**

The calculated electron density profiles of the calcite–$\text{NaCl}$ interfaces at 25, 45, and 80 °C are plotted in Figure 5. The electron density profiles were converted from the nuclear density distribution assuming that the electrons of atoms are located on their center. To directly compare the
profiles with the experimental results, a broadening procedure considering the limited maximum $Q$ values of experiments was conducted for the electron density profiles of the MD results. The MD simulation results revealed four maxima in the NaCl solution at $z = 2.5, 3.1, 4.9,$ and $7.0 \text{ Å.}$ A small decrease in density on the peaks was confirmed at $z = 3.1 \text{ Å}$ upon increasing the temperatures from 25 to 80 °C. The peaks at $z = 0$ and $-3 \text{ Å}$ in the calcite sample at 80 °C were smaller than the corresponding peaks at 45 and 25 °C. Such a change was attributed to the small shift in the positions of C and Ca to the interface at 80 °C and the larger width than those at low temperatures. The change in the peak position appears to be larger than that of the thermal vibration of ions estimated by the change in lattice parameters at a high temperature. We cannot conclude this for this reason here, but the balance of interactions between $\text{Ca}^{2+}$, $\text{CO}_3^{2-}$, and water molecules should be slightly changed at elevated temperatures.

**DISCUSSION**

Comparison of electron density profiles obtained from previous CTR experiments and MD simulations

Surface X-ray scattering measurements of low-salinity solutions have previously been taken at room temperature (Chiarello and Sturchio, 1995; Sturchio et al., 1997; Cheng et al., 1998; Fenter et al., 2000; Geissbühler et al., 2004; Heberling et al., 2011, Fenter and Sturchio, 2012; Fenter et al., 2013; Fenter et al., 2014; Callagon et al., 2014; Hofmann et al., 2016); however, it is useful to compare the electron density profiles for understanding the effect of salinity. Here, our results were compared with those from previous experiments by Heberling et al., which were conducted at room temperature for a dilute salt solution (Heberling et al., 2011) (Fig. 6). This experiment was selected because the spatial resolution determined by the maximum $Q$ value is similar to that in our experiments, and the major component of salt is NaCl. The peaks of the outermost calcite layer at $z = 0 \text{ Å}$ were lower and broader in our experiments than those of previous experiments that measured low salt concentrations. The peak height gradually decreased from 0.002 M to 0.5 m at $z = 0 \text{ Å}$. The obtained peak intensities of the solution in our experiments at $z = 2-4 \text{ Å}$ were higher than those in previous experiments. No subsequent peak at $z-6.2 \text{ Å}$ was reported in the previous study as their struc-
The experimental peak from 6 Å to the more relaxed structure of the outermost calcite layer obtained by the simulations and experiments for highly concentrated salt solutions (Heberling et al., 2011). The difference in the positions of the first peaks.

Elements at the interfaces interpreted by the MD simulations

The electron density profiles discussed so far have been interpreted as a component of the MD simulations. The height of the first peak at 4.9 Å is attributed to elements at the interfaces interpreted by the MD simulations and previous surface X-ray scattering measurements conducted for calcite-low-salinity aqueous solution interfaces (Heberling et al., 2011).

Comparison of the electron density profiles of the calcite-SNaCl interface at 25 °C obtained by our experimental best-fit model, MD simulations (broken line), and previous surface X-ray scattering measurements conducted for calcite-low-salinity aqueous solution interfaces (Heberling et al., 2011).

Comparison of the electron density profiles of the calcite-SNaCl interface at 80 °C calculated by the MD simulations (broken line) and experimental best-fit model (solid line).

MD simulations are useful for identifying specific molecular configurations at mineral-liquid interfaces that could be responsible for a particular electron density profile, because the experimental electron density profiles only contain indirect information about the specific atomic species at the interface. Therefore, the MD simulations can be used to interpret the experimental results. There was no significant difference between the experiments and simulations at 80 °C; therefore, the electron density profiles at 80 °C were consistent with those of the experiments. The differences between the peak positions obtained by the simulations and experiments for the NaCl solution at z ≥ 0 Å could be due to the small structural change in the calcite surface observed by the CTR experiment. There was a small difference between the peak positions obtained by the simulations and experiments for the NaCl solution at z ≥ 0 Å. The difference could be due to the more relaxed structure of the outermost calcite layer in the experiments at z ≥ 0 Å than that predicted by the MD simulations. The height of the first peak of the MD results at z = 2.5 Å was similar to that of the experiments at z = 3.2 Å, therefore, the first MD peak corresponds to the first peak of the experiment at z = 3.2 Å. The second MD peak at 4.9 Å can be interpreted as a component of the experimental peak from 6–8 Å by considering the difference in the positions of first peaks.

The contributions of each ion to the total electron density profile at 80 °C are shown in Figure 8a. The NaCl solution at z ≥ 0 Å, the oxygen atoms in the water molecules contribute the largest component of the electron density profile, while the hydrogen atoms contribute very little (Figs. 8a and 8b). Contributions from NaCl are only observed near the calcite surface i.e. for z < 6 Å, even though a high salt concentration of 0.5 mol/kg was employed to simulate seawater. The first peak at z = 2.5 Å in the NaCl solution was attributed to the H2O molecules adsorbed on the calcite’s surface, while the second peak at z = 3.1 Å was formed by the adsorbed H2O molecules, Cl, and Na+. The third peak at z = 4.9 Å is attributed to the H2O molecules and Cl−. The number densities of ions (Fig. 9) show that the Cl− and Na+ are concentrated near the calcite’s surface. The Na+ formed a single peak near the surface, while the Cl− formed two peaks near the surface, which is similar to the results reported previously for highly concentrated salt solutions (Chen et al., 2015). The contribution of the density of two Cl− peaks into the number density plot is 0.0060 (Å−2), which is almost equal to that of the single Na+ peak, which was 0.0062 (Å−2). The adsorbed Na+ corresponds to an inner-sphere complex (Figs. 10a and 10b). The first Cl− peak corresponds to an inner-sphere complex, as shown in Figures 10c and 10d. The second peak is the outer sphere complex of Cl−, as shown in Figures 10e and 10f. These differences could originate from the properties of the calcite surface, because no significant differences were reported for the free hydration energies of Na+ (−365 kJ/mol) and Cl− (−340 kJ/mol) (Marcus, 1991). The difference could be explained by the stronger hydration energy of Ca2+.
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(−1505 kJ/mol) on the surface than that of CO$_3^{2−}$ (−1315 kJ/mol) (Marcus, 1991). The formation of a hydration shell on the surface CO$_3^{2−}$ is less stable than that of Ca$^{2+}$, which then stabilizes the direct adsorption of Na$^+$ onto the surface CO$_3^{2−}$ without water.

In this study, we define the inner–sphere complex as the direct adsorption of ions onto the surface without the presence of water molecules between the surface and ions. Such an inner–sphere complex appears to have a strong chemical bond with the surface, but this is not the case for monovalent Na$^+$ and Cl$^−$. The major interaction between these monovalent ions, and the calcite surface is Coulombic, and no strong covalent bond is formed. The concept of the inner–sphere complex used in zeta–potential measurements, and surface speciation models is the presence of chemical bonds between the ions and mineral surface (Stumm, 1995). Therefore, it should be noted that the identification of inner–sphere
Na⁺ and Cl⁻ complexes by molecular simulations or direct experimental observations do not indicate the presence of inner-sphere complexes estimated by surface speciation models.

The presence of inner-sphere Na⁺ and Cl⁻ complexes has been reported at the interface of high-salinity water and calcite surface using MD simulations (Chen et al., 2015). This is consistent with our results. However, no inner-sphere complexes of these ions were reported at low salt concentrations of 0.25 M (Ricci et al., 2013). This may be due to differences in the force field. The CHARMM force field was used in the study using low salt concentrations (Ricci et al., 2013). No information was provided for the version of the CHARMM force field that they used, but the Charmm-27 version of the CHARMM force field overestimates the hydration energy when compared with experimental results and other common force fields such as Amber and OPLS (Patra and Karttunen, 2004). This suggests that the reproducibility of the dehydration of Na⁺ and Cl⁻ may be low for the model presented by Ricci et al. (2013). This may be a reason for the absence of inner-sphere complexes of these ions in their study.

The hydration number and residence time of water molecules in the first hydration shell of metal ions were calculated by the MD simulation, as listed in Table 4. The hydration numbers of ions in bulk water and surface ions were consistent with those in experiments (Ohtaki and Radnai, 1993; Badyal et al., 2004) and DFT studies (Sakuma et al., 2014). The residence time near Na⁺ and Cl⁻ in bulk water was consistent with previous experimental and theoretical values. The time was long for the surface ions in calcite, while that of surface CO₃²⁻ was shorter than that of surface Ca²⁺, indicating that the interaction between the surface CO₃²⁻ and water molecules was weaker than that of surface Ca²⁺. These results support the suggestion that the hydration shell of surface CO₃²⁻ is less stable than that of surface Ca²⁺. No significant difference was observed for the Cl⁻ peaks at different temperatures (25, 45, and 80 °C in Fig. 9). However, for Na⁺, a small decrease in the peak intensity was observed with decreasing temperature.

### Table 4. Hydration number of the first hydration shell and the residence time of water molecules

<table>
<thead>
<tr>
<th>Ions</th>
<th>Hydration number (MD)</th>
<th>Residence time (ps) (MD)</th>
<th>Residence time (ps) (previous studies)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺ in bulk water</td>
<td>5.6 ± 0.7</td>
<td>25 ± 3</td>
<td>27 (Bakker, 2008), 22.8 (Koneshan et al., 1998)</td>
</tr>
<tr>
<td>Cl⁻ in bulk water</td>
<td>5.9 ± 0.5</td>
<td>20 ± 2</td>
<td>15 (Bakker, 2008), 17.5 (Koneshan et al., 1998)</td>
</tr>
<tr>
<td>Ca²⁺ in bulk water</td>
<td>7.7 ± 0.8</td>
<td>&gt; 190</td>
<td>60 (Bakker, 2008), &lt;100 (Ohtaki and Radnai, 1993), 699 (Koneshan et al., 1998)</td>
</tr>
<tr>
<td>Surface Ca²⁺</td>
<td>1.0 ± 0.0</td>
<td>&gt; 474</td>
<td>–</td>
</tr>
<tr>
<td>Surface CO₃²⁻</td>
<td>1.5 ± 0.3</td>
<td>182 ± 180</td>
<td>–</td>
</tr>
</tbody>
</table>

Stability of surface Ca²⁺ and CO₃²⁻ under the presence of inner-sphere Na⁺ and Cl⁻ complexes

The pair-correlation functions (pcf) between the surface Ca and O or the surface C and O atoms of calcite are plotted in Figure 11. There is a clear difference in the pcf of Ca-O between the hydrated and Cl-adsorbed Ca²⁺. The averaged positions of Cl-adsorbed Ca²⁺ slightly shifted towards the NaCl solution, which could be a mechanism causing the decreased electron density peak intensity at the outermost calcite surface layer observed by the CTR measurements in Figure 6. In contrast, no difference between the Na-adsorbed CO₃²⁻ and hydrated CO₃²⁻ was observed for the pcf of C-O. The rate-limiting step in the dissolution of calcite could be associated with the solvent structure of Ca²⁺ (Pokrovsky and Schott, 2002). An AFM study found that the etch pit spreading rate of calcite increases when the background electrolyte of NaCl increases (Ruiz-Agudo et al., 2010). Our MD simulations suggested that the presence of inner-sphere Cl⁻ complexes destabilizes the surface Ca²⁺; this is opposite to the effect of Na⁺, which has no significant effect on the structure of surface CO₃²⁻. This could be due to the enhanced calcite dissolution rate under the presence of electrolytes in water observed in the AFM study (Ruiz-Agudo et al., 2010). This effect would be significant for highly concentrated salt solutions due to the increased number of surface-adsorbed Na⁺ and Cl⁻.

### Effect of adding Mg²⁺ and SO₄²⁻

The concentrations of the Mg²⁺ and SO₄²⁻ in the solution are much lower than those of Na⁺ and Cl⁻. The contributions of Na⁺ and Cl⁻ to the electron density profiles of the solution were limited, as shown in Figure 8a, therefore, the direct contributions from Mg²⁺ and SO₄²⁻ to those of the bulk solution should be limited unless these ions are concentrated at the calcite’s surface. Significant changes as a function of temperature in the electron density profiles of the system with the NaCl solution were observed. However, no significant temperature dependence was observed for the electron density of SNaCl-MgSO₄ from am-
The effects of Mg$^{2+}$ and SO$_4^{2-}$ on the structure of the outermost layer should be explored in future work.

CONCLUSIONS

The structures of calcite–0.5 m NaCl solution interfaces at a temperature of 25 to 80 °C, and pressure 0.1 MPa were studied by X-ray CTR scattering and classical molecular dynamics simulations. The differences in the CTR scattering profiles obtained at different temperatures could be attributed to relaxation of the outermost calcite surface, which may have occurred through the destabilization of the hydration shell of surface Ca$^{2+}$ and CO$_3^{2-}$ by the presence of a background electrolyte, Na$^+$ or Cl$^-$. The electron density profiles of a pure-NaCl solution were characterized by two peaks near the calcite surfaces. MD simulations suggested that these peaks arose from the presence of adsorbed water molecules, inner-sphere Na$^+$ complexes, and inner and outer sphere Cl$^-$ complexes. The density of adsorbed Na$^+$ exhibits a single peak, while the adsorbed Cl$^-$ formed two peaks near the calcite's surface. These can be explained by the differences in their interactions with surface CO$_3^{2-}$ and Ca$^{2+}$. The hydration energy of CO$_3^{2-}$ is smaller than that of Ca$^{2+}$, therefore, Na$^+$ is directly adsorbed onto the surface. The presence of inner-sphere Cl$^-$ complexes destabilizes surface Ca$^{2+}$, while the effect of Na$^+$ on the structure of surface CO$_3^{2-}$ is insignificant. The presence of MgSO$_4$ in the NaCl solution broadens the surface electron density profiles, compared with that of NaCl solution without MgSO$_4$.

ACKNOWLEDGMENTS

This study was performed under the cooperative research program of the Institute of Nature and Environmental Technology, Kanazawa University No. 11 (FY2013) and No. 5 (FY2014). This study has been carried out under approval of the Photon Factory Program Advisory Committee (Proposal Nos. 2012G047, 2014G117, 2016G067). This work was supported by JSPS KAKENHI Grant Number JP23740390. Travel and subsistence costs for the synchrotron experiments for HOS were funded by the Danish Agency for Science, Technology and Innovation via Danscatt.

SUPPLEMENTARY MATERIALS

Figures S1, S2, S3, and S4 and Tables S1 and S2 are available online from https://doi.org/10.2465/jmps.180329.

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Manuscript handled by Satoshi Utsunomiya

Manuscript received March 29, 2018
Manuscript accepted July 23, 2018