Iodate in calcite and vaterite: Insights from synchrotron X-ray absorption spectroscopy and first-principles calculations

J. Podder ^a, J. Lin ^a, W. Sun ^a, S. M. Botis ^a, J. Tse ^b, N. Chen ^c, Y. Hu ^c, D. Li ^d, J. Seaman ^e, & Y. Pan ^{a,*}

Abstract

Calcium carbonates such as calcite are the dominant hosts of inorganic iodine in nature and are potentially important for the retention and removal of radioactive iodine isotopes (¹²⁹I and ¹³¹I) in contaminated water. However, little is known about the structural environment of iodine in carbonates. In this study, iodate (IO₃⁻) doped calcite and vaterite have been synthesized using the gel-diffusion method at three NaIO₃ concentrations (0.002; 0.004; 0.008 M) and a pH value of 9.0, under ambient temperature and pressure. Inductively coupled plasma mass spectrometry (ICP-MS) analyses show that iodine is preferentially incorporated into calcite over vaterite. Synchrotron iodine K-edge X-ray absorption near-edge structure (XANES) spectra confirm that IO₃⁻ is the dominant iodine species in synthetic calcite and vaterite. Analyses of iodine K-edge extended X-ray absorption fine structure (EXAFS) data, complemented by periodic first-principles calculations at the density functional theory (DFT) levels, demonstrate that the I⁵⁺ ion of

the IO_3^- group in calcite and vaterite is bonded by three and two additional O atoms (i.e., coordination numbers = 6 and 5), respectively, and is incorporated *via* the charged coupled substitution $\text{I}^{5+} + \text{Na}^+ \leftrightarrow \text{C}^{4+} + \text{Ca}^{2+}$, with the Na^+ cation at a nearest Ca^{2+} site being the most energetically favorable configuration.

Keywords: Radionuclides; Calcite; Vaterite; Iodate; Synchrotron XAS; First-Principles Calculations.

1. INTRODUCTION

The retention of radionuclides is an important issue in order to maintain a safe environment for human and animal life as well as proper eco-system function. Among radionuclides, iodine (I) includes some of the most problematic radioisotopes in nuclear power production, nuclear fuel reprocessing and nuclear waste disposal due to their high solubility and high mobility. For example, the radioactive iodine ^{129}I , a β -emitter with a half-life of 15.7 million years, is released as a fission product during nuclear weapon tests and the operation of nuclear power facilities (Moran et al., 1999; McKeown et al., 2015; Riley et al., 2016). Also, ^{131}I (half-life = 8 days) along with ^{137}Cs (half-life = 30.17 years) are the most important risk drivers immediately after nuclear accidents such as those that occurred at Chernobyl and Fukushima (Yasunari et al., 2011; Laurencin et al., 2014).

Iodine is found in natural systems as iodide (I^- ; valence -1), iodate (IO_3^- ; +5), the elemental form iodine I_2 (valence 0) and organic-bound species. Although I^- and IO_3^- are both monovalent anions, they show different sorption properties on marine sediments, soil minerals and humic substances, with IO_3^- sorbing to a greater degree than I^- (Francois, 1987; Ticknor et al., 1990; Hu et al., 2005; Kaplan et al., 2014). In nature,

most iodine is associated with inorganic carbonate minerals rather than organic matter (Muramatsu and Wedepohl, 1998; Claret et al., 2010). The long half-life and high environmental mobility of iodine combined with its biological activity in the thyroid make ^{129}I a significant environmental risk associated with nuclear waste storage and/or disposal (Moran et al., 1999; Altmann, 2009; Grambow, 2008; Riley et al., 2016). ^{129}I confinement can be achieved through sorption onto minerals and/or precipitation with the host mineral phases. Once ^{129}I enters the environment, it follows the behavior of stable ^{127}I , which is ubiquitous in nature. Therefore, it is important to understand the environmental behavior of both radioactive ^{129}I and stable ^{127}I in order to evaluate the fate of and possible health risks associated with ^{129}I (Yamaguchi et al., 2010).

Calcium carbonates, which are the major constituents of carbonate rocks and the most abundant biominerals, are present as several polymorphs, including calcite, aragonite and vaterite, as well as amorphous phases (Kato et al., 2002). The structures of calcite and vaterite contain ordered and disordered CO_3^{2-} planar triangular groups, respectively (Wang and Becker, 2009; Le Bail et al., 2011; Mugnaioli et al., 2012; Demichelis et al., 2012; 2013; Burgess and Bryce, 2015). Elevated levels of iodine have been documented to occur in both natural and synthetic calcium carbonates and are assumed to be present mainly as the IO_3^- group substituting for CO_3^{2-} (Lu et al., 2010; Lerouge et al., 2010; Zhang et al., 2013). Also, the I/Ca values in marine carbonates have been proposed as a geochemical proxy for constraining ancient seawater redox change and climate change in general, because iodine is a redox-sensitive element and has been suggested to involve the $\text{IO}_3^- \leftrightarrow \text{I}^-$ conversion in seawater (Lu et al., 2010; Zhou et al., 2014). However, little is known about the substitution mechanism of the much larger IO_3^- pyramidal group for the CO_3^{2-} planar triangle in calcium carbonates.

In this study, IO_3^- doped calcite and vaterite have been synthesized at ambient temperature and pressure. These samples were characterized using a suite of analytical techniques from scanning electron microscopy (SEM) to powder X-ray diffraction (PXRD) analysis, inductively coupled plasma mass spectrometry (ICP-MS), electron microprobe analysis (EMPA), single-crystal and powder electron paramagnetic resonance (EPR) spectroscopy, magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy, and synchrotron X-ray absorption spectroscopy (XAS). Synchrotron XAS data, in particular, have been analyzed and interpreted with complementary results from periodic density functional theory (DFT) calculations, providing a molecular-level understanding of the chemical speciation, substitution mechanisms and local structural environments of iodine in calcium carbonates.

2. MATERIALS AND METHODS

2.1. Synthesis and characterization of iodate doped calcite and vaterite

The single- and double-diffusion methods with sodium metasilicate gel (Lin et al., 2013a,b; Lin et al., 2014) have been modified to synthesize IO_3^- doped calcite and vaterite. The starting materials included analytical grade sodium metasilicate (Na_2SiO_3 ; 18 mesh granular and purity $\geq 95.0\%$ Alfa Aesar), calcium chloride (CaCl_2 ; 99.99 % BDH), ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$; 99.9% BDH), sodium iodate (NaIO_3 ; 99.99% Sigma-Aldrich), acetic acid (Sinopharm chemical reagent, $\geq 99.5\%$) and Milli-Q water (18.2 $\text{M}\Omega\cdot\text{cm}$ at 25 °C). A stock solution was first prepared by adding 2.5 g Na_2SiO_3 in 50 mL of deionized water, stirred for about 30 minutes, and then left undisturbed for 30 minutes. The clear solution was then filtered using Whatman filter paper (11 μm pore

size) and stored. Subsequently, a 1 M acetic acid solution was prepared and stirred for 15 minutes. The Na_2SiO_3 solution was added drop wise to 50 mL of 1 M acetic acid using a burette, while constantly stirring the solution to prepare the Na_2SiO_3 gel with a specific gravity of approximately 1.05 g/cm^3 . Ammonium carbonate solutions of 0.16 M concentration were impregnated into the gel solution of equal volumes. Also, NaIO_3 at the concentrations of 0.002, 0.004 and 0.008 M was added to the gel solution separately. The solutions were then transferred into several amorphous silica tubes by allowing the mixture to fall steadily along the walls of the tubes to avoid the formation of air bubbles. After the gel settled, 20 mL of 0.16 M CaCl_2 was poured over the gel to initiate nucleation. The tubes were then sealed with Parafilm to prevent evaporation and gel contamination. The solutions turned into translucent gels after a few hours of equilibration. All runs had a pH value of approximately 9.0 and the stoichiometric ratio of $\text{Ca}^{2+}/\text{CO}_3^{2-} = 1$. The nucleation and growth processes were very slow, with only a small number of crystals found after three to four weeks.

The solid products, after washing with deionized water and drying in air, were first examined under a binocular microscope and were hand-picked to separate calcite and vaterite for further characterization. However, the amounts of vaterite obtained from the runs with 0.002 M and 0.004 M NaIO_3 were exceedingly small to permit any detailed analyses. The separates of synthetic products (3 calcite and 1 vaterite) were then examined using a JEOL 840 SEM to document crystal morphology and surface features, and were also analyzed on a PANalytical X'pert PRO X-ray diffractometer (Cu $K\alpha 1$ radiation $\lambda = 1.5406 \text{ \AA}$ at 40 kV and 45 mA). The bulk iodine contents of calcite and vaterite from the 0.008 M NaIO_3 run, after dissolution in HF-HNO_3 , were determined by ICP-MS analyses. Also, five calcite crystals from this run were mounted in a pyrex plug

and polished for EMPA analyses on a JEOL JXA-8600 Superprobe. The microprobe was operated at a 15 kV excitation voltage, a ~50 nA beam current, a ~10 μm beam diameter, and a counting time of 60 s, with calcite, albite and synthetic $\text{Na}_8(\text{Al}_6\text{Ge}_6\text{O}_{24})\text{I}_2$ (Fleet, 1989) as standards. Interferences of the Ca K_β X-ray peak on the iodine L_α and L_β lines (see also Calret et al., 2010) were evaluated using a diopside standard and were corrected for off-line.

Synthetic calcite from the run with 0.008 M NaIO_3 (i.e., before and after washing with deionized water) as well as the starting material NaIO_3 were analyzed for ^{23}Na MAS NMR, using a Bruker AVANCE III HD spectrometer operating at 132.29 MHz, with a 4 mm DOTY CP-MAS probe and an MAS rate of 6 kHz. A 90° pulse of 2.15 μs and a recycle delay of 2 s were used for the ^{23}Na MAS experiments (no ^1H decoupling), at a total of 32 and 1024 scans for NaIO_3 and calcite, respectively. Chemical shifts are referenced to 1M NaCl aqueous solution at 0 ppm.

2.2. Synchrotron X-ray absorption spectroscopy

Synchrotron iodine K-edge (33,169 eV) spectra of synthetic calcite (from runs at 0.002, 0.004 and 0.008 M NaIO_3) and vaterite (0.008 M) as well as selected model compounds (NaI , NaIO_3 and $\text{Ca}(\text{IO}_3)_2$) were measured at the Hard X-ray MicroAnalysis beamline (HXMA) at the Canadian Light Source (Saskatoon, Canada). At the HXMA beamline, a monochromatic beam was produced using a pair of Si (III) monochromator crystals with the second crystal detuned by 50% of fully tuned beam reduction of harmonic; and Rh mirror was introduced in this experiment. To improve signal-to-noise ratios in the XANES and EXAFS data, the number of scans was increased for each of the iodine doped samples to account for the low iodine concentration. The samples of

147 synthetic calcite and vaterite were mounted in aluminum holders, which were covered
148 with kapton at a 45° angle with respect to the incident X-ray beam and were placed
149 between the I_0 and I_t ion chambers. For energy calibration purposes, a third ‘reference’
150 ion chamber (I_R) was downstream of the I_t chamber, where the crystalline I_2 standard was
151 placed between I_t and I_R detectors so that transmission data for this standard was
152 collected in parallel with the fluorescence and transmission data for each sample. The
153 synthetic samples were measured in the fluorescence mode using a 32-element solid state
154 Ge detector positioned at 90° to the X-ray beam. The samples were held at 8 K using an
155 Oxford Instruments liquid helium flow cryostat to reduce the beam damage, and straight
156 ion chamber detectors filled with standard > 99.99 % nitrogen gas. The absorption
157 coefficient (μ) of the samples at a particular energy was proportional to I_f/I_0 ; and the
158 corresponding μ of the iodine standard at each energy was $-\ln(I_R/I_t)$. The X-ray
159 absorption spectrum is shown as a plot of μ versus energy in eV, with an uncertainty of
160 ± 2 eV.

161 Each XAS spectrum was processed using standard pre-edge background
162 subtraction and edge-step normalization procedures (Sayers and Bunker, 1998). The K-
163 absorption edge first derivative inflection point in each I_2 calibration spectrum was set to
164 33,169 eV and defined as E_0 for each XANES spectrum for the sample. After
165 normalization and calibration, direct comparisons can be made with XANES data for all
166 the samples with an accuracy of ± 2 eV, or the energy difference between two adjacent
167 data points at the K-edge. The iodine K-edge EXAFS $k^2 \cdot \chi(k)$ data of calcite and vaterite
168 have been analyzed for R space curve fittings using the software FEFF7 (Rehr and Albers,
169 2000) and WinXas 3.2 (Ressler, 1997). Fourier transform was performed using a

Gaussian window function over the k range of 2.95 to 12.03 Å⁻¹ and the R-space fitting windows of 0.74-2.93 Å.

2.3. First-principles calculations

All first-principles calculations utilized the supercell approach and various DFT methods, including Becke's three-parameter (B3) hybrid density functional methods B3LYP/B3PW (Becke, 1993) as implemented in CRYSTAL09 (Dovesi et al., 2009) and the parameter free hybrid method PBE0 (Adamo & Barone, 1999). Previous calculations showed that these DFT methods describe crystalline structures satisfactorily (Li and Pan, 2011; Zhao et al., 2013). All-electron basis sets used for Na, H, C, Ca and O were those of the triple-zeta valence plus polarization (TZVP) quality (Peintinger et al., 2013), and the Hay-Wadt large core pseudopotential was used for iodine (<http://www.crystal.unito.it/basis-sets.php>). The thresholds for the overlap and penetration Coulomb integrals, the overlap for Hartree-Fock (HF) exchange integrals, and the two pseudo-overlaps for HF series were set to 10⁻⁶, 10⁻⁶, 10⁻⁶, 10⁻⁶, and 10⁻¹² hartree, respectively, while a SCF tolerance of 10⁻⁶ hartree was chosen. The Pack-Monkhorst shrink factor for the supercell geometry optimization was set to 6, corresponding to the total k points of 112 in the irreducible Brillouin zone.

Calculations started with the construction and optimization of the supercells for the perfect structures of calcite (80, 120 and 160 atoms), vaterite (60 and 120 atoms), and aragonite (80 atoms). The experimental unit-cell parameters and atomic coordinates of Maslen et al. (1993) were used in the initial model of calcite. Numerous structures involving varying degrees of disorder proposed for vaterite (Wang and Becker, 2009; Le

Bail et al., 2011; Mugnaioli et al., 2012; Demichelis et al., 2012; 2013; Burgess and Bryce, 2015) have been evaluated as the initial models in this study, and that with the space group $C2/c$ (Mugnaioli et al., 2012) was found to be the most stable and was selected for calculations with I for C substitutions. The experimental unit-cell parameters and atomic coordinates of Dal Negro and Ungaretti (1971) were used in the initial model of aragonite.

Iodine was then introduced into the central C site(s) in the optimized supercells by three types of charge-coupled substitutions: $\text{IO}_3^- + \text{Na}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$, $\text{IO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$, and $2\text{IO}_3^- + \text{V}_{\text{Ca}} \leftrightarrow 2\text{CO}_3^{2-} + \text{Ca}^{2+}$, where V_{Ca} denotes a vacancy at a Ca site. Several calculations were done for each of these substitutions at different I-Na, I-H and I- V_{Ca} distances as the initial models. Calculations involving the substitutions $\text{IO}_3^- + \text{Na}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$ and $\text{IO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$ were made with the supercells of 60, 80, 120 and 160 atoms to evaluate the effect of the supercell sizes. All calculations for the substitution $2\text{IO}_3^- + \text{V}_{\text{Ca}} \leftrightarrow 2\text{CO}_3^{2-} + \text{Ca}^{2+}$ were made with the supercells of 120 and 160 atoms.

Calculations for all three substitutions $\text{IO}_3^- + \text{Na}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$, $\text{IO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$, and $2\text{IO}_3^- + \text{V}_{\text{Ca}} \leftrightarrow 2\text{CO}_3^{2-} + \text{Ca}^{2+}$ were made by the addition and removal of neutral atoms. Therefore, these substitution reactions can be re-written as $\text{I} + \text{Na} \leftrightarrow \text{C} + \text{Ca}$, $\text{I} + \text{H} \leftrightarrow \text{C} + \text{Ca}$, and $2\text{I} + \text{V}_{\text{Ca}} \leftrightarrow 2\text{C} + \text{Ca}$, respectively. The formation energies (E^f) of the IO_3^- group in calcite, vaterite and aragonite can then be calculated by the equations $E^f = E^d + E_{\text{Ca}} + E_{\text{C}} - E^p - E_{\text{Na}} - E_{\text{I}}$, $E^f = E^d + E_{\text{Ca}} + E_{\text{C}} - E^p - E_{\text{H}} - E_{\text{I}}$, and $E^f = E^d + E_{\text{Ca}} + 2E_{\text{C}} - E^p - 2E_{\text{I}}$, respectively (Mallia et al., 2001; Li and Pan, 2011). Here, E^p and E^d denote the energies of the perfect and defective systems, respectively. E_{Ca} , E_{C} , E_{Na} ,

E_H and E_I represent the energies of the Ca, C, Na, H and I atoms, respectively, and were calculated using the same basis sets and functionals.

3. RESULTS

3.1. Characterization of iodate-doped calcite and vaterite

The as-grown calcite crystals are of the characteristic rhombohedral shape up to 2 mm in the maximum dimension (Fig. 1a). The vaterite aggregates are spherical in shape (Fig. 1b) and are characterized by porous surfaces (Fig. 1c). At the NaIO₃ concentrations above 0.1 M, large crystals (up to 3 mm in the maximum dimension) of lautaerite (Ca(IO₃)₂) formed (Fig. 1d). Highly pure crystals of calcite, as confirmed by PXRD analyses (Fig. S1), were readily separated from the solid products. PXRD analyses of iodate-doped calcite from the run at 0.008 M NaIO₃ yielded unit-cell parameters: $a = 4.997(2)$ Å and $c = 17.070(5)$ Å, larger than those ($a = 4.9939(2)$ and $c = 17.051(1)$ Å) of iodate-free calcite that was synthesized in the same way but without NaIO₃ in the starting solution. However, the vaterite separates often contain small amounts of calcite (Fig. S1).

ICP-MS analyses showed that the iodine contents in calcite and vaterite synthesized at 0.008 M NaIO₃ are $8,980 \pm 430$ (n=3) and $1,990$ mg kg⁻¹, respectively. The iodine content in calcite is significantly higher than the maximum value reported in biogenic carbonates (Lerouge et al., 2010) but is generally consistent with that extrapolated from previous calcite-water experiments at lower iodine concentrations (Lu et al., 2010). Electron microprobe analyses showed that the iodine content in calcite

varies significantly both in individual grains and between crystals (0.64 ± 0.22 wt.%; $n = 17$) and exhibits a positive correlation with Na_2O close to the Na:I atomic ratio of 1:1 (Fig. 2), suggesting a charge coupled substitution $\text{IO}_3^- + \text{Na}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$ (see below). The origin of this large variation in the I content in calcite is unclear, and back-scattered electron (BSE) imaging analyses did not detect any iodate-rich inclusions. Attempts of EMPA analyses for iodine and Na_2O in synthetic vaterite were unsuccessful due to both the small grain sizes (Fig. 1c) and low abundances.

The millimeter-sized crystals of calcite were originally intended for single-crystal electron paramagnetic resonance (EPR) spectroscopic investigation, which can provide unambiguous evidence for lattice-bound iodine (Lin et al., 2013a,b; Pan and Nilges, 2014). Unfortunately, single-crystal and powder EPR measurements of synthetic calcite and vaterite, with and without gamma-ray irradiation, did not detect any paramagnetic ^{127}I -associated species (nuclear spin = $5/2$ and 100% natural isotope abundance; Symons and Misra, 1981; Anusuya et al., 1992). This result is probably attributable to the presence of Mn^{2+} (confirmed by the characteristic ^{55}Mn hyperfine structure in EPR spectra; Fig. S2) and other transition metal impurities in the synthetic samples, which may represent deeper electron traps than the IO_3^- species (thus preventing the conversion of the diamagnetic IO_3^- to paramagnetic species during gamma-ray irradiation). Nevertheless, the large crystal sizes combined with vigorous washing in an ultrasonic bath apparently minimized iodine sorption on the surfaces of calcite. Also, optical microscopic examination together with back-scattered electron imaging on the JEOL JXA-8600 Superprobe did not detect any iodine-rich inclusions in the calcite crystals. Similarly, surface sorption on vaterite was probably minimized by vigorous washing in an ultrasonic bath as well. The fact that the powder sample of vaterite with large surface

areas contains only ~20% iodine in the calcite crystals from the same synthesis experiment also points to limited surface sorption.

Figure 3 shows that the ^{23}Na MAS NMR spectrum of as-is calcite (i.e. without washing in deionized water) is characterized by two small signals at ~7 ppm and ~1 ppm, whereas that of this sample after washing has only a weak broad signal centered at -2 ppm. The signal at ~1 ppm is probably attributable to an aqueous species (e.g., Na^+ in fluid inclusions?). The signal at ~7 ppm is similar to that of the starting material NaIO_3 and may represent to NaIO_3 sorped on the surface of calcite crystals, because it is absent in the washed sample. The broad signal of synthetic calcite after vigorous washing has an apparent second-order quadrupole lineshape but cannot be reasonably fitted with a single Na species. Spectral fitting with two Na species (i.e., inclusion of an aqueous species similar to that in the as-is sample) yielded an isotropic chemical shift δ_{iso} of -2.5 ppm, a nuclear quadrupole coupling constant C_Q of 1.6 MHz and an asymmetry parameter η_Q of 0.2.

3.2. Synchrotron XANES and EXAFS spectra

Figure 4 shows the synchrotron iodine K-edge XANES spectra of synthetic calcite and vaterite, in comparison with those of the model compounds. The XANES spectra of both calcite and vaterite showed no visible changes between scans, suggesting no beam-induced oxidation or reduction during the data collection. The XANES spectra confirm that IO_3^- is the dominant iodine species in both synthetic calcite and vaterite (Fig. 4).

The synchrotron iodine K-edge EXAFS data of synthetic calcite and vaterite are all dominated by one broad peak in the R space (Fig. 5). These EXAFS data can be fitted first for the IO_3^- group with three O atoms at ~1.81 Å (Tables 1 and 2), similar to those

from other EXAFS studies of iodates (Laurencin et al., 2014; McKeown et al., 2015). This value is also in excellent agreement with the average $\langle \text{I-O} \rangle$ bond distance of 1.8106(77) Å for the IO_3^- groups in iodate minerals from single-crystal X-ray structure refinements (Mi and Pan, 2016).

On the basis of theoretical calculations (see below), subsequent fittings included three and two O atoms in the second path for calcite and vaterite, respectively (Tables 1 and 2). The O atoms in the second path were either grouped together (i.e., Model I) or allowed to vary independently (Model II). We emphasize that Model II is not fully justified by the experimental EXAFS data but is included for comparison with Model I and theoretical results (Tables 3 and 4). Table 1 clearly shows that the fitted results for the three iodate-doped calcite samples synthesized at different NaIO_3 concentrations are similar, suggesting no change in the iodine coordination environment with the iodine content. Also, the quality of our measured EXAFS data does not warrant interpretation beyond these two paths. The fitted EXAFS results of the two reference compounds NaIO_3 and $\text{Ca}(\text{IO}_3)_2$ are given in supplementary data (Fig. S3 and Table S1).

3.3. First-principles calculations

Theoretical calculations for the substitution $\text{IO}_3^- + \text{Na}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$, using both the hybrid density functional methods B3LYP/PW91 and the parameter free hybrid method PBE0, can predict the formation of the classic IO_3^- group with one short single I-O bond and two long I=O double bonds in calcite (Table 3), vaterite and aragonite (Table 4). Generally, calculation results using the supercells of different sizes (80, 120 and 160 atoms for calcite, and 60 and 120 atoms for vaterite) are similar. The average $\langle \text{I-O} \rangle$ bond distance of the calculated IO_3^- groups is ~ 1.83 Å (Tables 3 and 4), which is ~ 0.02 Å or

~2% larger than those from the EXAFS analyses (Tables 1 and 2). It is interesting to note that calculations using other functionals (e.g., Wu and Cohen, 2006; Bilc et al., 2008) or those using the pseudopotential of Doll and Stoll (1998) for iodine yielded even larger overestimates for the <I-O> bond distances (Table 3). Also, previous theoretical calculations of iodates, using the projector augmented wave method and plane wave basis sets as implemented in the Vienna Ab Initio Simulation Package (VASP), overestimated the <I-O> bond distances by similar amounts (Laurencin et al., 2014).

The most energetically favorable configurations for the substitution $\text{IO}_3^- + \text{Na}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$ in calcite, vaterite, and aragonite are all those obtained from the initial models with the Na-I pairs at the nearest Ca and C sites. The substitution of the much larger IO_3^- pyramidal group for the CO_3^{2-} planar triangles is accompanied by a marked displacement of the I atom from the original C position after structural optimizations. This displacement leads to a relaxed Na-I distance of ~ 3.70 Å (Table 3), significantly larger than the original Ca-C distance of 3.21 Å in calcite (Maslen et al., 1993) but comparable to that (3.47 Å) of the nearest Na-I distance in NaIO_3 (Svensson and Stahl, 1988). The calculated ^{23}Na nuclear quadrupole coupling constant C_Q and the asymmetry parameter η_Q from the PBE0 method (Table 3) are in best agreement with those obtained from the ^{23}Na MAS NMR spectrum (Fig. 3). Similarly, the relaxed Na-I distance for the most stable iodate-doped vaterite is 3.64 Å, in comparison with the original Ca-C distance of 3.12 Å (Mugnaioli et al., 2012). The IO_3^- pyramidal group in calcite is surrounded by three additional O atoms at distances between ~ 2.75 and ~ 2.85 Å (Table 3; Fig. 6a), different from the local structural environment of only three O atoms in the first shell for the C atom in calcite. Similarly, the IO_3^- pyramidal group in vaterite has two additional O atoms at 2.56 and 3.04 Å (Table 3; Fig. 6b). The relaxed Na-I distance for

the most stable iodate-doped aragonite is 3.51 Å (Table 4), in comparison with the original Ca-C distance of 2.91 Å (Dal Negro and Ungaretti, 1971). The IO_3^- pyramidal group in aragonite is also surrounded by three additional O atoms at distances between ~2.89 and ~2.95 Å (Table 4).

Similarly, calculations for the substitution $\text{IO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$ with the I and H atoms at distant C and Ca sites, respectively, in the initial models yielded the classic IO_3^- groups in both calcite (Table 3) and vaterite (Table 4). However, the initial models with the nearest H-I pairs gave the most energetically stable configuration for this substitution, consisting of two short I-O bonds at ~1.83 Å and one long I-O bond (~2.0 Å) linked to the H atom (i.e., an HOIO_2 pyramidal group; Fig. 6c; Tables 3 and 4). This HOIO_2 pyramid differs from the IO_3^- group but is similar to the iodic acid configuration (Krauzman et al., 1973; Drougas and Kosmas, 2005; Nelyubina et al., 2011; Hou et al., 2013). The HOIO_2 pyramids in calcite and vaterite are both surrounded by two additional O atoms at ~2.47 Å to ~2.75 Å (Tables 3 and 4). Calculations for the substitution $\text{IO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$ in aragonite were not successful.

For the substitution $2\text{IO}_3^- + \text{V}_{\text{Ca}} \leftrightarrow 2\text{CO}_3^{2-} + \text{Ca}^{2+}$, models with different initial I-I and I- V_{Ca} distances (e.g., a vacancy at the nearest Ca site from one or two I atoms, and a vacancy at a Ca site away from both I atoms), can all stabilize the IO_3^- groups in both calcite (Table 3) and vaterite (Table 4). However, the most energetically favorable configuration again comes from the initial models with two nearest I atoms next to a Ca vacancy. From this model one of the calculated IO_3^- groups in calcite and vaterite features one short I-O and two long I-O bonds, similar to those of the IO_3^- predicted from the substitution $\text{IO}_3^- + \text{Na}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$. However, the second IO_3^- group in calcite is significantly asymmetrical, with three different I-O bonds (Table 3). Asymmetrical

IO₃⁻ groups have been reported to occur in crystalline iodates (Ghose et al., 1978; Svensson and Stahl, 1988; Burns and Hawthorne, 1993; Mi and Pan, 2016). The two IO₃⁻ groups in both calcite and vaterite are also surrounded by three additional O atoms each and share two common O atoms to form the [I₂O₁₀] dimer (Fig. 6d).

4. DISCUSSION

4.1. Substitution mechanisms of iodate in calcite and vaterite

The slow “gel diffusion” synthesis technique adopted in the present study was intended to minimize adsorption/extrapement that has been shown to occur in supersaturation coprecipitation experiments (Heberling et al., 2014) and to grow large crystals of calcite for characterizations. BSE imaging and EMPA analyses did not detect any inclusion of iodate-rich phases, and PXRD and ²³Na MAS NMR data provide further support for the incorporation of iodate and Na in the calcite lattice.

Electron microprobe data (Fig. 2) and synchrotron K-edge XANES spectra (Fig. 4) suggest that IO₃⁻ is the dominant iodine species in calcite and is incorporated mainly by the substitution IO₃⁻ + Na⁺ ↔ CO₃²⁻ + Ca²⁺. Sodium ions were readily available in our synthesis experiments, because NaIO₃ was used as starting materials in the Na₂SiO₃ gel. This substitution is further supported by agreements between synchrotron iodine K-edge EXAFS data (Tables 1 and 2) and theoretical calculations (Tables 3 and 4) and by similar ²³Na nuclear quadrupole parameters from MAS NMR experiments (Fig. 3) and theoretical predictions (Table 3).

Closer inspection of Figure 2 shows that more than half of the EMPA data points (10/17) lie below the Na:I=1:1 line. This apparent Na deficiency is attributable to either the analytical uncertainty of EMPA or the presence of additional substitution(s) for IO₃⁻ incorporation in synthetic calcite. First-principles calculations show that the substitution

$\text{IO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$ is energetically favorable in comparison with $\text{IO}_3^- + \text{Na}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$ in both calcite and vaterite (Tables 3 and 4). Also, this substitution with distant I and H atoms leads to the IO_3^- group observed in synchrotron iodine K-edge XANES and EXAFS data. However, the most energetically favorable HOIO_2 geometries predicted for the substitution $\text{IO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$ (Tables 3 and 4) are not consistent with the synchrotron iodine K-edge EXAFS data. The dominant contribution of the substitution $\text{IO}_3^- + \text{Na}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$ to the IO_3^- incorporation in calcite investigated in this study (Fig. 2) is probably attributable to the high pH condition used in the synthesis experiments, because the substitution $\text{IO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$ is pH dependent and may become important under more acidic conditions.

Our first-principles calculations show that the substitution $2\text{IO}_3^- + \text{V}_{\text{Ca}} \leftrightarrow 2\text{CO}_3^{2-} + \text{Ca}^{2+}$ is less energetically favorable than the other two (Tables 3 and 4). Nevertheless, this substitution may be possible in calcite formed at high temperatures, where Ca vacancies have been suggested to occur (Cygan et al., 2002; Sun et al., 2012).

4.2. Local structural environments of iodate in calcite and vaterite

Although synchrotron iodine K-edge EXAFS data of calcite and vaterite do not provide information beyond the first coordination shell of the I^{5+} ion, first-principles calculations predict that the most energetically favorable configurations are those with the charge coupling ion (i.e., Na^+) linked directly to the IO_3^- groups (Fig. 6a,b). These configurations were obtained from the initial models with the nearest Na-I pairs, pointing to the importance of maintaining the local electrostatic neutrality.

First-principles calculations support synchrotron iodine K-edge EXAFS data that the IO_3^- groups in calcite and vaterite differ significantly from the CO_3^{2-} planar triangles and

are characterized by linkages to three and two additional O atoms, forming the six-fold and five-fold coordination polyhedra (Tables 1 and 2; Fig. 6a,b). These irregular coordination polyhedra of the iodine atoms in calcite and vaterite are consistent with the stereochemistry of I^{5+} containing the lone-pair electrons, which require the three nearest O atoms located on the other side. In natural and synthetic iodates, the IO_3^- groups are commonly bonded to one or more additional O atoms on the side of the lone-pair electrons to form a variety of four-fold to eight-fold coordination polyhedra (Ghose et al., 1978; Svensson and Stahl, 1988; Burns and Hawthorne, 1993; Mi and Pan, 2016). Therefore, the six-fold and five-fold coordination polyhedra of iodine in calcite and vaterite (Fig. 6a,b) are similar to those in iodates.

4.3. Implications for the uptake of iodate in calcite, vaterite and aragonite

Lu (2013) pointed out that understanding of lattice-bound IO_3^- in calcite is particularly important for remediation purposes, because it is more resistant to remobilization than absorbed iodine and organic varieties. However, previous discussions of IO_3^- incorporation in calcite were based on only crystal-chemical and geochemical considerations (Lu et al. 2010; Zhang et al., 2013). The present study provides the first spectroscopic data as well as theoretical predictions for the substitution mechanisms and local structural environments of IO_3^- in calcite and vaterite.

Another interesting result of this study is that IO_3^- is preferentially incorporated into calcite over vaterite, although the thermodynamic relationship between these two minerals in our synthesis experiments is difficult to evaluate. The difference in the predicted formation energy (ΔE^f) of the IO_3^- group between calcite and vaterite, when the same substitution and the same method are used, becomes: $\Delta E^f = (E^d - E^p)_{\text{vaterite}} - (E^d -$

E^p_{calcite} . In all the models evaluated for the substitution $\text{IO}_3^- + \text{Na}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$, the ΔE^f values are ≥ 0.48 eV. Also, the ΔE^f values for the substitution $\text{IO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$ are positive, pointing to calcite being more efficient than vaterite in the uptake of IO_3^- in aqueous environments over a range of pH values.

Zhang et al. (2013) noted that the addition of Na_2CO_3 (and subsequent CaCl_2) to the contaminated groundwater at the Hanford Site (Washington, USA) promoted calcite precipitation, which was accompanied by a reduction in the IO_3^- concentration as well as an increase in pH. However, the calcite precipitation induced by Na_2CO_3 removed only 0.3-2.7% of the aqueous iodine, much less than that observed at lower pH conditions. Zhang et al. (2013) interpreted these results to a pH impedance of IO_3^- incorporation into calcite. The present study shows that the pH impedance observed by Zhang et al. (2013) can be explained by the substitution $\text{IO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$. Therefore, our first-principles calculations provide the molecular mechanism for asserting that pH manipulation of contaminated aquifers is a possible remediation strategy for ^{129}I (Zhang et al. 2013). Also, the possible incorporation of the iodic acid HOIO_2 species in calcite and vaterite under acidic conditions (Fig. 6c) is intriguing but requires further experimental studies for confirmation.

Finally, first-principles calculations suggest that the substitution with $\text{IO}_3^- + \text{Na}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$ in aragonite is energetically least favorable among the three CaCO_3 polymorphs (Tables 3 and 4). Further experimental studies are needed to confirm or refute this theoretical prediction.

5. CONCLUSIONS

The incorporation of IO_3^- in two CaCO_3 polymorphs, calcite and vaterite, was investigated in a series of synthesis experiments at three NaIO_3 concentrations (0.002, 0.004 and 0.008 M) and a pH value of ~ 9.0 , under ambient temperature and pressure. These experiments show that iodine is preferentially incorporated into calcite over vaterite. Synchrotron iodine K-edge XANES spectra confirm that IO_3^- is the dominant iodine species in both calcite and vaterite. Analyses of K-edge EXAFS data and periodic first-principles calculations show that the IO_3^- group in calcite and vaterite is linked to three and two additional O atoms (i.e., CN = 6 and 5), respectively, and is incorporated *via* the charged coupled substitution $\text{IO}_3^- + \text{Na}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$, with the Na^+ cation at a nearest Ca^{2+} site being the most energetically favorable configuration. Our first-principles calculations for the substitution $\text{IO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$ also provide a molecular mechanism for pH control on the uptake of IO_3^- in calcite.

ACKNOWLEDGEMENTS

We thank Drs. Jean-Francois Boily, Frank Heberling, and two anonymous reviewers for incisive criticisms and helpful suggestions. We also thank the Sylvia Fedoruk Canadian Centre for Nuclear Innovation for financial support, Canadian Light Source for access to synchrotron XAS experiments, WestGrid Computing Facilities of Compute Canada for providing resources for DFT calculations, and Dr. Jianfeng Zhu for assistance with ^{23}Na MAS NMR analyses. JCS's participation in this study was supported by the U. S. Department of Energy under Award Numbers DE-FC09-07SR22506 to the University of Georgia Research Foundation.

REFERENCES

- Adamo C. and Barone V. (1999) Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **110**, 6158–6170.
- Altmann S. (2009) Geochemical research: A key building block for nuclear waste disposal safety cases. *J. Contam. Hydrol.* **102**, 174-179.
- Anusuya B., Murty V. S. and Rama Rao K. V. S. (1992) Electron spin resonance study on single crystals of orthoperiodic acid γ irradiated at room temperature. *J. Phys. Condens. Matter.* **5**, 3681-3688.
- Becke A. D. (1993) A new mixing of Hartree-Fock and local density-functional theories. *J. Chem. Phys.* **98**, 1372–1377.
- Bilc D. I., Orlando R., Shaltaf R., Rignanese G. M., Iniguez J. and Ghosez Ph. (2008) Hybrid exchange-correlation functional for accurate prediction of the electronic and structural properties of ferroelectric oxides. *Phys. Rev. B* **77**, 165107.
- Burgess K. M. N. and Bryce D. L. (2015) On the crystal structure of the vaterite polymorph of CaCO_3 : A calcium-43 solid-state NMR and computational assessment. *Solid State Nucl. Magn. Reson.* **65**, 7-83.
- Burns P. C. and Hawthorne F. C. (1993) The crystal structure of dietzeite, $\text{Ca}_2\text{H}_2\text{O}(\text{IO}_3)_2(\text{CrO}_4)$, a heteropolyhedral framework structure. *Can Mineral.* **31**, 313-319.
- Claret F., Lerouge C., Lauriou T., Bizi M., Conte T., Ghestem J. P., Wille G., Sato T., Gaucher E. C., Giffaut E. and Tournassat C. (2010) Natural iodine in a clay formation: Implications for iodine fate in geological disposals. *Geochim. Cosmochim. Acta* **74**, 16-29.
- Cygan R. T., Wright K., Fidler D. K., Gale J. D. and Slater B. (2002) Atomistic models of carbonate minerals: Bulk and surface structures, defects, and diffusion. *Mol. Simul.* **28**, 475-495.
- Dal Negro A. and Ungaretti L. (1971) Refinement of the crystal structure of aragonite. *Am. Mineral.* **56**, 768-772.
- Demichelis R., Raiteri P., Gale J. D. and Dovesi R. (2012) A new structural model for disorder in vaterite from first-principles calculations. *CrystEngComm* **14**, 44-47.
- Demichelis R., Raiteri P., Gale J. D. and Dovesi R. (2013) The multiple structures of vaterite. *Cryst. Growth Des.* **13**, 2247-2251.
- Doll K. and Stoll H. (1998) Ground-state properties of heavy alkali halides. *Phys. Rev. B* **57**, 4327-4331.

- Dovesi R., Saunders V. R., Roetti C., Orlando R., Zicovich-Wilson C. M., Pascale F., Civalieri B., Doll K., Harrison N. M., Bush I. J., D'Arco Ph. and Llunell M. (2009) CRYSTAL09 User's Manual, University of Torino, Torino, Italy.
- Drougas E. and Kosmas A. M. (2005) Computational studies of (HIO₃) isomers and the HO₂ + IO reaction pathways. *J. Phys. Chem. A* **109**, 3887-3892.
- Fleet M. E. (1989) Structures of sodium aluminogermanate sodalites [Na₈(Al₆Ge₆O₂₄)A₂, A = Cl, Br, I]. *Acta Crystallogr. C* **45**, 843-847.
- Francois R. (1987) The influence of humic substances on the geochemistry of iodine in nearshore and hemipelagic marine sediments. *Geochim. Cosmochim. Acta* **51**, 2417-2427.
- Ghose S., Wan C. and Wittke O. (1978) The crystal structure of synthetic lautarite, Ca(IO₃)₂. *Acta Cryst. B* **34**, 84-88.
- Grambow B. (2008) Mobile fission and activation products in nuclear waste disposal. *J. Contam. Hydrol.* **102**, 180-186.
- Heberling F., Vinograd V. L., Polly R., Gale J. D., Heck S., Rothe J., Bosbach D., Geckeis H. and Winkler B. (2014) A thermodynamic adsorption/entrapment model for selenium(IV) coprecipitation with calcite. *Geochim. Cosmochim. Acta* **134**, 16-38.
- Hou G.-L., Wu M. M., Wen H., Sun Q., Wang X.-B. and Zheng W.-J. (2013) Photoelectron spectroscopy and theoretical study of M(IO₃)₂⁻ (M=H, Li, Na, K): Structural evolution, optical isomers, and hyperhalogen behavior. *J. Chem. Phys.* **139**, 044312.
- Hu Q., Zhao P., Moran J. E. and Seaman J. C. (2005) Sorption and transport of Iodine species in sediments from the Savannah River and Hanford Sites. *J. Contam. Hydrol.* **78**, 185-205.
- Kaplan D. I., Denham M. E., Zhang S., Yeager C., Xu C., Schwehr K. A., Li H. P., Ho Y. F., Wellman D. and Santschi P. H. (2014) Radioiodine biogeochemistry and prevalence in groundwater. *Crit. Rev. Environ. Sci. Technol.* **44**, 2287-2335.
- Kato T., Sugawara A. and Hosoda N. (2002) Calcium carbonate-organic hybrid materials. *Adv. Mater.* **14**, 869-877.
- Krauzman M., Le Postollec M. and Mathieu J. P. (1973) Vibration spectra, structure, and angular dispersion of phonons in crystalline iodic acid (α-HIO₃). *Phys. Stat. Sol. (b)* **60**, 761-768.
- Laurencin D., Vantelon D., Briois V., Gervais C., Coulon A., Grandjean A. and Campayo L. (2014) Investigation of the local environment of iodate in hydroxyapatite by combination of X-ray absorption spectroscopy and DFT modeling. *RSC Adv.* **4**, 14700-14707.

- Le Bail A, Ouhenia S. and Chateigner D. (2011) Microtwinning hypothesis for a more ordered vaterite model. *Powder Diffr.* **26**, 16-21.
- Lerouge C., Claret F., Denecke M. A., Wille G., Falkenberg G., Ramboz C., Beny C., Giffaut E., Schäfer T., Gaucher E.C. and Tournassat C. (2010) Comparative EPMA and μ -XRF methods for mapping micro-scale distribution of iodine in biocarbonates of the Callovian–Oxfordian clayey formation at Bure, Eastern part of the Paris Basin. *Phys. Chem. Earth* **35**, 271–277.
- Li Z. and Pan Y. (2011) First-principles study of boron oxygen hole centers in crystals: Electronic structures and nuclear hyperfine and quadrupole parameters. *Phys. Rev. B* **84**, 115112.
- Lin J., Chen N., Nilges M. J. and Pan Y. (2013a) Arsenic speciation in synthetic gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$): A synchrotron XAS, single-crystal EPR and pulsed ENDOR study. *Geochim. Cosmochim. Acta* **106**, 524-540.
- Lin J., Chen N. and Pan Y., (2013b) Arsenic incorporation in synthetic struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$): A synchrotron XAS and single-crystal EPR study. *Environ. Sci. Technol.* **47**, 12728-12735.
- Lin J., Chen N. and Pan Y. (2014) Arsenic speciation in newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) determined by synchrotron X-ray absorption and electron paramagnetic resonance spectroscopies: implications for the fate of arsenic in green fertilizers. *Environ. Sci. Technol.* **48**, 6938-46.
- Lu Z. (2013) Comment on “Iodine-129 and iodine-127 speciation in groundwater at the Hanford Site, U.S.: Iodate incorporation into calcite”. *Environ. Sci. Tech.* **47**, 13203–13204.
- Lu Z., Jenkyns H. C. and Rickaby R. E. M. (2010) Iodine to calcium ratios in marine carbonate as a paleo-redox proxy during oceanic anoxic events. *Geology* **38**, 1107-1110.
- Mallia G., Orlando R., Roetti C., Ugliengo P. and Dovesi R. (2001) F center in LiF: A quantum mechanical ab initio investigation of the hyperfine interaction between the unpaired electron at the vacancy and its first seven neighbors. *Phys. Rev. B* **63**, 235102.
- Maslen E. N., Streltsov V.A. and Streltsova N. R. (1993) X-ray study of the electron density in calcite, CaCO_3 . *Acta Crystallogr. B* **49**, 636-641.
- McKeown D. A., Muller I.S. and Pegg I. L. (2015) X-ray absorption studies of iodine valence and local environments in borosilicate waste glasses. *J. Nucl. Materials* **456**, 182-191.

- Mi J.-X. and Pan Y. (2016) Halogen rich minerals: Crystal chemistry and geological significance. In "Role of Halogens in Terrestrial and Extraterrestrial Processes", D. Harlov, ed., Springer.
- Moran J. E., Oktay S., Santschi P. H. and Schink D. R. (1999) Atmospheric dispersal of ¹²⁹Iodine from nuclear fuel reprocessing facilities. *Environ. Sci. Tech.* **33**, 2536–2542.
- Mugnaioli E., Andrusenko I., Schuler T., Loges N., Dinnebier R. E., Panthofer M., Tremel W. and Kolb U. (2012) Ab-initio-strukturbestimmung von vaterit mit automatischer beugungstomographie. *Angew. Chem.* **124**, 1-6.
- Muramatsu Y. and Wedepohl K. H. (1998) The distribution of iodine in the earth's crust. *Chem. Geol.* **147**, 201-206.
- Nelyubina Y. V., Autipin M. Y. and Lyssenko K. A. (2011) Extremely short halogen bond: the nature and energy of iodine-oxygen interactions in crystalline iodic acid. *Mendel. Commun.* **21**, 250-252.
- Pan Y. and Nilges M. J. (2014) Electron paramagnetic resonance (EPR) spectroscopy: Basic principles, experimental techniques and applications to Earth and planetary sciences. *Rev. Mineral. Geochem.* **78**, 655-690.
- Peintinger M. F., Vilela Oliveira D. and Bredow T. (2013) Consistent gaussian basis sets of triple-zeta valence with polarization quality for solid-state calculations. *J. Comput. Chem.* **34**, 451-459.
- Rehr J. J. and Albers R. C. (2000) Theoretical approaches to x-ray absorption fine structure. *Rev. Mod. Phys.* **72**, 621-654.
- Ressler T. (1997) WinXAS: A new software package not only for the analysis of energy-dispersive XAS data. *J. de Phys. IV* **7**, 269-270.
- Riley B. J., Vienna J. D., Strachan D. M., McCloy J. S. and Jerden J. L. Jr. (2016) Materials and processes for the effective capture and immobilization of radioiodine: A review. *J. Nucl. Mat.* **470**, 407-426.
- Sayers D. E. and Bunker B. A. (1988) Data analysis. In X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES, Eds. Koningsberger, D. C., and Prins, R., John Wiley, New York, pp.211-253.
- Sun Z., Luo S., Qi P. and Fan L.-S. (2012) Ionic diffusion through calcite (CaCO₃) layer during the reaction of CaO and CO₂. *Chem. Eng. Sci.* **81**, 164-168.
- Svensson C. and Stahl K. (1988) The crystal structure of NaIO₃ at 293K. *J. Solid State Chem.* **77**, 112-116.

- Symons M. C. R. and Misra S. P. (1981) Electron-gain and -loss centres in irradiated periodates: an electron spin resonance study. *J. Chem. Soc. Dalton Trans.* 2183-2187.
- Ticknor K.V. and Cho Y. H. (1990) Interaction of iodide and iodate with granitic fracture filling minerals. *J. Radioanal. Nucl. Chem.* **140**, 75-90.
- Wang J. and Becker U. (2009) Structure and carbonate orientation of vaterite (CaCO_3). *Am. Mineral.* **94**, 380-386.
- Wu Z. G. and Cohen R. E. (2006) More accurate generalized gradient approximation for solids. *Phys. Rev. B* **73**, 235116.
- Yamaguchi N., Nakano M., Takamatsu R. and Tanida H. (2010) Inorganic iodine incorporation into soil organic matter: evidence from iodine K-edge X-ray absorption near-edge structure. *J. Environ. Radioact.* **101**, 451-457.
- Yasunari T. J., Stohl A., Hayano R. S., Burkhart J. F., Eckhardt S. and Yasunari T. (2011) Cesium-137 deposition and contamination of Japanese soils due to the Fukushima nuclear accident. *Proc. Natl. Acad. Sci. U.S.A.* **108**, 19530–19534.
- Zhao, B.-C., Sun, W., Ren, W.-J., Huang, Y.-X., Li, Z., Pan, Y. and Mi, J.-X. (2013) Hygroscopic $\text{La}[\text{B}_5\text{O}_8(\text{OH})]\text{NO}_3 \cdot 2\text{H}_2\text{O}$: Insight into the evolution of borate fundamental building blocks. *J. Solid State Chem.* **206**, 91-98.
- Zhang S., Xu C., Creeley D., Ho Y-F., Li H.-P., Grandbois R., Schwehr K. A., Kaplan D. I., Yeager C. M., Wellman D. and Santschi P. H. (2013) Iodine-129 and iodine-127 speciation in groundwater at the Hanford Site, U.S.: Iodate incorporation into calcite. *Environ. Sci. Tech.* **47**, 9635–9642.
- Zhou X., Thomas E., Rickaby R. E. M., Winguth A. M. E. and Lu Z. (2014) I/Ca evidence for upper ocean deoxygenation during the PETM. *Paleocean.* **29**, 964-975.

FIGURE CAPTIONS

Figure 1. SEM images of (a) typical iodate doped calcite crystals obtained from 0.008 M NaIO_3 , (b) spherical aggregates of vaterite, (c) surface features of vaterite, and (d) lautaerite crystal ($\text{Ca}(\text{IO}_3)_2$) produced from 0.16 M NaIO_3 .

Figure 2. EMPA data (solid squares) showing a positive correlation between Na_2O and I contents in calcite synthesized at 0.008 M NaIO_3 . The dashed line at the Na:I atomic ratio of 1:1 is drawn for comparison.

Figure 3. ^{23}Na MAS NMR spectra of calcite synthesized at 0.008 M NaIO_3 (“as-is” denotes no washing; “washed”, washing with deionized water in an ultrasonic bath). Also shown for comparison is that of the starting material NaIO_3 .

Figure 4. Iodine K-edge XANES spectra of synthetic calcite (0.002 M, 0.004 and 0.008 M NaIO₃) and vaterite (0.008 M NaIO₃), in comparison with those of model compounds NaI, NaIO₃ and Ca(IO₃)₂.

Figure 5. R-space curve fittings for iodine K-edge EXAFS spectra of calcite (a) and vaterite (b) from 0.008 M NaIO₃. Fourier transforms of $k^2 \cdot \chi(k)$ spectra were performed over the k ranges of 2.95-12.03 Å⁻¹ and R-space fitting windows of 0.74-2.93 Å.

Figure 6. The iodine coordination polyhedra in calcite (a) and vaterite (b) predicted from DFT calculations using the IO₃⁻ + Na⁺ ↔ CO₃²⁻ + Ca²⁺ substitution. Also shown that Na is linked to an O atom of the IO₃⁻ group in both calcite and vaterite; (c) the HOIO₂ configuration with two additional O atoms in calcite predicted from the IO₃⁻ + H⁺ ↔ CO₃²⁻ + Ca²⁺ substitution with the nearest H-I pair; and (d) the [I₂O₁₀] dimer in calcite from the 2IO₃⁻ + V_{Ca} ↔ 2CO₃²⁻ + Ca²⁺ substitution.

Figure 1

Figure 2

730
731
732

Figure 3

Figure 4

Figure 5

Figure 6

746 Table 1. Local structural environments of I^{5+} in calcite from iodine K-edge EXAFS
747

Sample	0.002 M			0.004 M			0.008 M		
Paths	CN	R(Å)	$\sigma^2(\text{Å}^2)$	CN	R(Å)	$\sigma^2(\text{Å}^2)$	CN	R(Å)	$\sigma^2(\text{Å}^2)$
Model I									
1 (O1-3)	3.0 ^a	1.81	0.0022	3.0 ^a	1.81	0.0023	3.0 ^a	1.81	0.0019
2 (O4-6)	3.0 ^a	2.78	0.01 ^b	3.0 ^a	2.75	0.01 ^b	3.0 ^a	2.80	0.01 ^b
Residual	12.63%			11.67%			9.43%		
E ₀ (eV)	8.0 ^b			8.0 ^b			8.0 ^b		
Model II									
1 (O1-3)	3.0 ^a	1.81	0.0022	3.0 ^a	1.81	0.0021	3.0 ^a	1.81	0.0019
2 (O4)	0.7	2.60	0.0032	0.8	2.60	0.0022 ^b	0.5	2.57	0.0019 ^b
2 (O5)	0.8	2.75	0.0089	1.4 ^b	2.79	0.0022 ^b	1.4 ^b	2.76	0.0066
2 (O6)	1.1	2.81	0.009 ^b	1.2	3.01	0.0022 ^b	0.7	3.01	0.01 ^b
Residual	7.61%			4.12%			4.24%		
E ₀ (eV)	8.0 ^b			8.0 ^b			8.0 ^b		

748
749 The amplitude reduction factor S_0^2 is 1.0. The uncertainty of the interatomic distance R is
750 ± 0.02 Å. ^a and ^b denote the parameters fixed and constrained, respectively, during fitting.
751

752
753 Table 2. Local structural environments of I^{5+} in vaterite from iodine K-edge EXAFS
754

Paths	CN	R(Å)	$\sigma^2(\text{Å}^2)$
Model I			
1 (O1-3)	3.0 ^a	1.81	0.0022
2 (O4-5)	2.0 ^a	2.90	0.01 ^b
Residual	8.30%		
E ₀ (eV)	8.0 ^b		
Model II			
1 (O)	3.0 ^a	1.80	0.0021
2 (O4)	0.7	2.71	0.0057
2 (O5)	1.2	2.90	0.0057 ^b
Residual	6.66%		
E ₀ (eV)	8.0 ^b		

755
756 The amplitude reduction factor S_0^2 is 1.0. The uncertainty of the interatomic distance R is
757 ± 0.02 Å. ^a and ^b denote the parameters fixed and constrained, respectively, during fitting.
758

Table 3. Local structural environments of I^{5+} in calcite from DFT calculations

Substitution	I + Na						I + H		2I + V _{Ca}	
Supercell	80					120	120		160	
DFT	PBE0	B3LYP	B3PW	B1WC	B3PW*	B3PW	B3PW		B3PW	
I-Na/H/I (Å)	3.696	3.705	3.701	3.708	3.703	3.701	2.646	4.622‡	3.401	
I-O1 (Å)	1.8241	1.8301	1.8282	1.8651	1.8570	1.8253	1.8386	1.8255	1.8227	1.8347
I-O2	1.8416	1.8481	1.8463	1.8726	1.8756	1.8445	1.8407	1.8466	1.8443	1.8526
I-O3	1.8421	1.8492	1.8476	1.8832	1.8764	1.8458	1.9655	1.8487	1.8855	1.8535
I-O4	2.7647	2.7953	2.7480	2.7330	2.7457	2.7655	2.4701	2.7471	2.7015	2.5877
I-O5	2.8018	2.8394	2.7984	2.7410	2.7899	2.7868	2.6372	2.7913	2.7236	2.6519
I-O6	2.8070	2.8395	2.8016	2.7556	2.7949	2.8027		2.8423	2.8340	2.8906
C _Q (MHz) ^ε	1.55	1.42	1.38	1.41	1.37	1.38				
η _Q ^ε	0.14	0.12	0.08	0.11	0.09	0.10				
E [†] (AU)	0.6755	0.6543	0.6568	0.6689	0.9360	0.6569	0.6278	0.6358	1.3417	

Three substitutions $I + Na \leftrightarrow C + Ca$, $I + H \leftrightarrow C + Ca$ and $2I + V_{Ca} \leftrightarrow 2C + Ca$. B1WC, is the hybrid functionals of Wu and Cohen (2006) and Bilc et al. (2008); *, using the iodine pseudopotential of Doll and Stoll (1998); ‡, from a distant H-I pair in the initial model; ^ε, ²³Na nuclear quadrupole parameters. AU, atomic unit (1 AU = 1 hartree = 27.21 eV).

Table 4. Local structural environments of I^{5+} in vaterite and aragonite from DFT calculations

Mineral	Vaterite						Aragonite		
Substitution	I + Na		I + H			2I + V _{Ca}	I + Na		
Supercell	60	120	60	120	120	120	80		
DFT	B3PW	B3PW	B3PW	B3PW	B3PW	B3PW	B3PW		
I-Na/H/I (Å)	3.639	3.640	2.512	2.513	4.998‡	4.075	3.5145	6.8857	
I-O1 (Å)	1.8365	1.8369	1.8252	1.8251	1.8323	1.8183	1.8197	1.8257	1.8104
I-O2	1.8421	1.8419	1.8275	1.8282	1.8457	1.8442	1.8566	1.8381	1.8380
I-O3	1.8423	1.8421	2.0335	2.0331	1.8468	1.8538	1.8676	1.8423	1.8389
I-O4	2.5652	2.5641	2.6453	2.6439	2.5666	2.6976	2.6400	2.8883	2.8957
I-O5	3.0356	3.0376	2.7450	2.7448	3.0279	3.0342	3.0821	2.9294	2.9506
I-O6						3.0727	3.1008	2.9502	3.0071
E [†] (AU)	0.6742	0.6743	0.6459	0.6458	0.6574	1.3516	0.6856	0.7010	

Three substitutions $I + Na \leftrightarrow C + Ca$, $I + H \leftrightarrow C + Ca$ and $2I + V_{Ca} \leftrightarrow 2C + Ca$. ‡, from a distant H-I pair in the initial model. AU, atomic unit (1 AU = 1 hartree = 27.21 eV).