Fluorine incorporation into calcite, aragonite and vaterite CaCO$_3$: Computational chemistry insights and geochemistry implications

Xiaolei Feng[a,b], Zvi Steiner[c,b,*], Simon A. T. Redfern[d,*]

[a]*Institute for Disaster Management and Reconstruction, Sichuan University - Hong Kong Polytechnic University, Chengdu, 610207, China*
[b]*Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, UK*
[c]*GEOMAR Helmholtz Centre for Ocean Research, Kiel, 24105 Germany*
[d]*Asian School of the Environment, Nanyang Technological University, 639798 Singapore*

Abstract

The abundant occurrence of calcium carbonate minerals in marine sediments and their high fluorine content suggests that fluorine is a good candidate for reconstructing paleoceanographic parameters. However, the potential of fluorine as a paleoproxy had hardly been explored, and fundamental insights into the behaviour of fluorine in biogenic carbonates and marine sediments is required. A first-principles modelling approach is used here to analyse the incorporation mechanisms of fluorine into crystalline calcium carbonates. We compute F incorporation into the CaCO$_3$ lattice via a number of mechanisms, but concentrate on comparison of the energetics of the two easiest substitution mechanisms: replacing one oxygen atom within the carbonate group to form a $(CO_2F)^-$ group as against a substitution involving replacement of the CO$_3$ group by two fluorine ions to form a CaF$_2$ defect. These incorporation mechanisms are fundamentally different from that of iodine into calcium carbonates, where a carbon atom is replaced. Our simulations suggest that the substitution of CO$_3^{2-}$ by F$_2^{2-}$ is the most favoured and that fluorine is preferentially incorporated into the three naturally-occurring polymorphs of calcium carbonate in the order vaterite $\gtrapprox$

*Corresponding authors
Email addresses: `zsteiner@geomar.de` (Zvi Steiner), `simon.redfern@ntu.edu.sg` (Simon A. T. Redfern)

aragonite $\gg$ calcite. These results explain the previously-reported preponderance of fluorine in aragonite corals, and lend support to the use of F/Ca as a proxy for ocean $p\text{CO}_2$.

Keywords: first-principles, fluorine, calcium carbonates, F/Ca ratios, marine chemistry

1. INTRODUCTION

Halogens play a number of important roles in the Earth system, both in Earth's ecosystems as well as a key component of many geochemical processes at Earth's surface. For example, they are a major constituent of the oceans, but in addition volcanic emissions of halogens are frequently considerable. Fluorine is unique among the halogens as it is the only such element that is preferentially enriched in Earth's mantle over seawater. The main sink for fluorine in the modern ocean is as an impurity in biogenic calcium carbonates (CaCO_3) and its enrichment in CaCO_3 exceeds chlorine by a factor of 10^5 (Carpenter, 1969). Fluorine concentrations in biogenic aragonites vary between 500 to 1600 ppm (Ramos et al., 2005; Tanaka & Ohde, 2010; Tanaka et al., 2013), making it one of the most abundant impurities in this carbonate mineral phase. Biogenic low-magnesium calcites typically contain 75 to 600 ppm fluorine (Opdyke et al., 1993; Rosenthal & Boyle, 1993), and the fluorine content of biogenic calcites increases as a function of the magnesium content of the calcite (Ohde & Kitano, 1980) (Kendrick, 2018).

The distinction between the F/Ca ratios of the various CaCO_3 polymorphs, and the large differences between the F/Ca ratio of calcium carbonates and other common fluorine-containing minerals (e.g. fluorapatite and fluorite), suggests the potential of using fluorine concentrations in seawater and CaCO_3 shells to understand past and present ocean environments. This potential has indeed been successfully realised in studies of mineral precipitation and dissolution occurring during early diagenesis in shallow marine sediments (Green & Aller, 2001; Rude & Aller, 1991). In theory, seawater concentrations of fluorine can

also be used in studies of global biogeochemistry. For example, Steiner et al. (2014, 2018) demonstrated how variations in seawater concentrations of strontium and calcium can be used to quantify the contributions of coral reefs and pelagic plankton to the $CaCO_3$ cycle of the Red Sea, based on the tendencies of various groups of calcareous organisms to incorporate strontium into their skeletons. Since fluorine concentrations also vary between skeletons precipitated by different groups of organisms, measurements of seawater concentrations of fluorine can be used to improve our understanding of the marine $CaCO_3$ cycle of the modern ocean and, for example, monitor the effects of ocean acidification on various groups of organisms.

Despite the promising prospect fluorine offers for marine sciences and paleoceanographic studies, alongside the fact that the fluorine concentrations in $CaCO_3$ shells are relatively high, the application of fluorine concentrations as indicators in environmental studies is very limited at present. The main reason for this is that the mechanism by which fluorine is incorporated into $CaCO_3$ is relatively poorly understood and there are no reliable predictions of how the incorporation of fluorine should change with varying environmental conditions. This problem is exemplified by the fact that there is no experimental evidence to show any correlation between the fluorine content of, for example, foraminiferal tests and the surface salinity and temperature of seas in which they grow. Instead, fluorine contents seem to vary according to the preferred depth of calcification of individual foraminifera species (Opdyke et al., 1993; Rosenthal & Boyle, 1993; Rosenthal et al., 1997). A recent study of laboratory-cultured benthic foraminifera suggests that the carbonate ion concentration of the growth medium is the only environmental parameter that co-varies with the fluorine content of foraminifera shells Roepert et al. (2019).

Though we cannot rule out the possibility of surface adsorption and interstitial site incorporation, there are solid lines of experimental evidence to suggest that the structural incorporation of fluorine into the crystallographic lattice sites of carbonates is dominant, but the incorporation mechanism is unclear and has been the subject of some debate. For example, Carpenter (1969) suggested

3

that fluorine is primarily incorporated into the calcium carbonate crystal structure, and the form in which the fluorine is present is unresolved. The data from Rosenthal & Boyle (1993) support the notion that fluorine occupies lattice sites, although the nature of this substitution and its fundamental controls were not specified. Ohde & Kitano (1980) and Kitano & Okumura (1973) suggested that the incorporation of fluorine into high-Mg calcites might be coupled with the co-precipitation of Mg, while Ichikuni (1979) suggested that the incorporation of fluorine into the crystalline structure of aragonite occurs by substitution of a carbonate ion by two fluorine ions during crystal growth:

$$CaCO_3(s) + 2F^-(aq) \Rightarrow CaF_2(s) + CO_3^{2-}(aq) \tag{1}$$
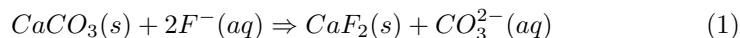
This substitution balances the charge of the substituting anions and was termed a "CaF$_2$" substitution. It should be understood, however, that it is not a substitution of fluorite itself, somehow incorporated into the calcium carbonate structure. Rather, the reaction following equation 1 involves the replacement of one CO$_3^{2-}$ oxy-anion in the carbonate structure by two F$^-$ anions. The relatively high partition coefficient of fluorine in aragonite (0.54-1.26) suggests that fluorine is likely to be incorporated into aragonite (and possibly other carbonate polymorphs) via some such mechanism, although other simpler ionic substitutions cannot be ruled out.

Here, we provide a systematic exploration and examination of potential mechanisms of fluorine substitution into the three common biomineral polymorphs of calcium carbonate, namely calcite, aragonite and vaterite. We use first-principles quantum mechanical *ab initio* structure calculations to obtain the structural and thermodynamic properties of fluorine-bearing carbonates and to explore the mechanism by which the main polymorphs of CaCO$_3$ might incorporate fluorine. Our calculations correspond to conditions of zero pressure and temperature, in common with previous such investigations of carbonates (e.g. Archer et al. (2003)), but are the first step in providing insights into the ground state thermodynamic properties of competing trace element incorporation mechanisms.

4

2. COMPUTATIONAL MODELS AND METHODS

2.1. Starting structures of $CaCO_3$

Three common polymorphs of calcium carbonate, $CaCO_3$, namely calcite, aragonite and vaterite, are all considered in this work. The starting structures for the computational work on calcite, aragonite and vaterite were those crystallising in space groups $R\bar{3}c$, $Pnma$, and Cc respectively. The structures of $R\bar{3}c$ calcite and $Pnma$ aragonite are well-known and indeed were among the first to be identified in the early history of X-ray crystallographic studies. We used the structures from Graf (1961) and De Villiers (1971) as starting points for our calculations. The structure of vaterite is much-debated as it appears to occur in a number of competing metastable polymorphs, and we therefore did not use any of the experimentally-derived structures. We choose, instead, the theoretically calculated Cc structure, containing 12 formula units of $CaCO_3$ per unit cell (Demichelis et al., 2013), for the convenience of making a supercell containing the same number of atoms for all three polymorphs.

2.2. Super-cells of $CaCO_3$

The incorporation of fluorine into pure calcium carbonate is treated as an impurity substitutional defect. Calculations were carried out with periodic boundary conditions. Such computational methods demand a balance between having a set of atoms (the simulation box) that is large enough such that the local strains associated with the incorporation of a defect are insignificant at its boundaries, with the constraint that the simulation box needs to be computational tractable in the context that the computational cost can scale as N^3, where N is the number of atoms. Thus, in order to have a simulation box large enough that periodically repeating fluorine substitutional defects are sufficiently distant that interactions between them are insignificant, a super-cell containing 24 formula units of $CaCO_3$ (120 atoms) was constructed for each of the polymorphs. We found that a simulation box (the super-cell) containing 120 atoms was large enough to accommodate any local structural distortion induced by

5

the fluorine, within its periodic boundaries, thus allowing us to model impurity incorporation without periodic boundary effects playing a role.

In the case of calcite, a super-cell was chosen that corresponds to four conventional hexagonal unit cells. The super-cell was, therefore, constructed as $2a \times 2b \times c$ where a, b, and c are the unit cell parameters of the hexagonal setting of the calcite $R\bar{3}c$ unit cell. For aragonite, the simulation box again contained 120 atoms and was comprised of a super-cell six times the volume of the conventional aragonite unit cell, constructed as $2a \times 3b \times c$, where a, b, and c are the unit cell parameters of the orthorhombic $Pnma$ unit cell of aragonite. For vaterite, the simulation box was twice the volume of the conventional vaterite unit cell, with a super-cell constructed as $a \times 2b \times c$, with a, b, and c being the cell parameters of the monoclinic Cc unit cell of vaterite.

2.3. Structure of fluorine-bearing CaCO$_3$

The periodic models of fluorine-bearing CaCO$_3$ were built, for structural optimisation, by introducing one fluorine atom into the CaCO$_3$ supercell and substituting one atom out, in three different substitution mechanisms. The first involved the substitution of a fluorine atom for calcium (Ca-site), onto the large octahedral site. The second corresponds to the substitution of fluorine for carbon (C-site), as a FO_3^- replacing the carbonate group, as observed in the case of iodine substitution (Podder et al., 2017; Feng & Redfern, 2018). The third involved the substitution of a fluorine atom for oxygen atom (O-site), forming $(CO_2F)^-$ groups. In each case the modified structures correspond to an average site occupancy of around 4% substitution of fluorine onto the site. In addition, we tested the "CaF$_2$" incorporation mechanism by introducing two fluorines into the structure and substituting this pair of F^- anions for a CO_3^{2-} group, with an initial starting configuration in which each fluorine was placed at the position of one of the three oxygens previously occupied in the carbonate group that had been removed. The substituted structures are constructed without imposing any symmetry restrictions, by starting from a set of atomic positions equivalent to the host phase but with the symmetry then reduced to $P1$, and

6

thus optimised under no symmetry restrictions, which means the full system geometry is relaxed. In many cases, there is more than one way to do the substitution, and all the structures reported here correspond to those with the lowest energies, having tested each option.

2.4. Structural optimisation

The energetics and physical properties of pure carbonates and fluorine-substituted phases were calculated using first-principles methods based on density functional theory, using periodic boundary conditions. Calculations are performed employing the Vienna *ab initio* simulation package (Kresse & Furthmüller, 1996). A kinetic energy cut-off of 520 eV was chosen after testing to ensure that it was large enough to arrive at converged reliable energies to less than 1 meV. Monkhorst-Pack meshes for Brillouin zone sampling were selected with a resolution of 0.3 Å^{-1} (see Supplementary Materials, Fig. S1). The generalised gradient approximation (Perdew et al., 1992) in the scheme of the Perdew-Burke-Enzerhoff (Perdew et al., 1996) pseudo-potentials was used, alongside projected-augmented-wave (PAW) potentials (Perdew et al., 1992, 1996) for electron-ion interactions. PAW potentials with $3s^2 3p^6 4s^2, 2s^2 2p^2, 2s^2 2p^4$, and $2s^2 2p^5$ electrons as valence electrons were adopted for the Ca, C, O and F atoms respectively.

We checked one set of F defect calculations against the energies of the pure (F-free) system to confirm whether dispersion corrections are required. The results of the three sets of calculations are listed in the Supplementary Materials (Table S1). Focusing on the O-site substitution, for example, we get the results as in Table S2, which demonstrate influence of dispersion corrections on our observations and we find it does not impact the relative enthalpy differences seen. With or without dispersion correction we still see that the relative enthalpies of vaterite $<$ aragonite $\ll$ calcite for the $(\text{CO}_2\text{F})^-$ group substitution are not affected and the introduction of dispersion corrections does not change our conclusions.

Note that the calculations do not assume the oxidation state of the halogen

Table 1: Energy increases (relative to pure components) due to fluorine incorporation in CaCO$_3$, calculated according to reactions 2, 3, 4 and 5. Units are kJ/mol (CaCO$_3$).

phase	Ca-site substitution	FO$_3$ defect	CO$_2$F defect	CaF$_2$ defect
calcite	42.13	40.47	13.22	-12.08
aragonite	41.37	39.09	7.57	-14.59
vaterite	35.82	32.53	5.56	-15.08

or other elements, but simply find the lowest enthalpy configuration based on the pseudo-potential model. Atomic relaxations were terminated when the change of the total energy per atom converged to within 1 meV per atom. All the calculations were conducted at ambient pressure and 0 K, which provides an insight into the ground state energies of the competing incorporation mechanisms. Crystal structures were plotted using VESTA, a programme for 3D visualisation of crystal structures and volumetric data (Momma & Izumi, 2011).

3. RESULTS

3.1. Enthalpies of fluorine-doped calcium carbonates

Using the relaxed structures as a starting point, the properties of fluorine-doped equivalents have been calculated either by introducing one fluorine atom into each of the supercells in the three substitution mechanisms specified by reactions 2, 3, and 4 below, or by introducing two fluorine atoms in place of the a carbonate group, following reaction 5. From the results of the calculations of energies, at zero temperature and pressure, of each of the relaxed structures fluorine-free and fluorine-bearing calcium carbonate structures, combined with the energies for elemental Ca, C, O and F under the same conditions, the energies associated with substitutional fluorine incorporation were determined. The following substitution schemes for all the three polymorphs (calcite, aragonite and vaterite) of CaCO$_3$ explain where the F is placed in the structure of calcite (it is important to understand that these equations are merely intended to

explain where the F is placed in the structure of calcite, and do not necessarily represent realistic substitution reactions):

$$24Ca(CO_3) + F \Rightarrow Ca_{23}F(CO_3)_{24} + Ca \tag{2}$$

$$24Ca(CO_3) + F \Rightarrow Ca_{24}(CO_3)_{23}(FO_3) + C \tag{3}$$

$$24Ca(CO_3) + F \Rightarrow Ca_{24}(CO_3)_{23}(CO_2F) + O \tag{4}$$

$$24Ca(CO_3) + F_2 \Rightarrow Ca_{23}(CO_3)_{23}(CaF_2) + CO_2 + O \tag{5}$$
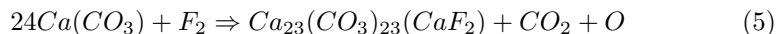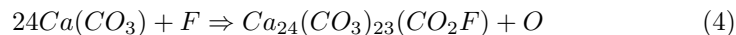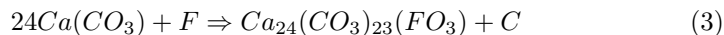
Incorporation of fluorine in calcium carbonates by the first three of these mechanisms is associated with some charge imbalance. In our calculations we have assumed a homogeneous electrostatic background. This corresponds to a mean field approach and, indeed, charge compensation may occur via substitutions that act over across much larger distances than those of our modelling simulation cell (including compensation at free surfaces). Given the very large number of possible coupled substitution mechanisms we have chosen not to attempt to explore individual potential mechanisms. The assumption of a homogeneous electrostatic background leads to reasonable description of the atomic-scale environment of the impurity, which is our main interest.

Calculated enthalpies for each of the reactants and products allow us to determine the reaction energies, at zero temperature and pressure, for each of these schemes in each of the three CaCO$_3$ polymorphs. The energies of these four reactions, calculated thus, are listed in Table 1. The energies associated with fluorine incorporation, as suggested by the calculation of the energies of $(CO_2F)^-$ defect and CaF$_2$ defect substituted compounds, for all three polymorphs, are significantly lower than the energies associated with Ca-site and C-site (or, FO$_3$ defect) fluorine substitutions. This result is very different from findings for iodine substitution into carbonates, where iodine is most easily accommodated

9

into calcium carbonates via C-site substitution, forming an iodate oxyanion group, IO_3^-, replacing the carbonate group (Feng & Redfern, 2018). It has previously been seen that reaction of fluorine ions with CO_2 to form $(CO_2F)^-$ is energetically feasible and has been experimentally observed (Bhargava & Balasubramanian, 2007), suggesting that such $(CO_2F)^-$ groups are indeed realistic species for potential incorporation into carbonates and that they might well be available in seawater for uptake by calcifying organisms. The substitution of two fluorine atoms onto two oxygen positions, and removal of the entire associated CO_3 group, is, however, even more favourable in our calculations. We find that the incorporation of this "CaF_2 defect", becomes exothermic and is significantly lower than the enthalpy of reaction of the $(CO_2F)^-$ substitution scheme for calcite, aragonite and vaterite. For both of these two lower-energy reaction schemes we find that substitution of fluorine into vaterite is slightly more easily accommodated than in aragonite, but that substitution of fluorine into calcite is far more difficult, indicated by the higher enthalpy of substitution.

Our calculations give the enthalpies of each of the structures of interest, that is, each of the tested modes of fluorine incorporation into calcite, aragonite and vaterite, relative to the fluorine-free equivalents. This provides the thermodynamic baseline against which geochemical incorporation mechanisms may be understood. Of course, each incorporation mechanism will, at elevated temperature, be associated with a further reduction in Gibbs energy due to entropic effects. Comparing the four reactions listed above we see that reactions 2 (Ca–F substitution) and 3 (C–F substitution) will be lower in entropy than reactions 4 and 5 (one, or two, F atom(s) replacing oxygen in the carbonate group, with or without removal of the remaining O and C atoms) since, for reactions 2 and 3 there is only one way to do the substitution, there being only one Ca or C in the formula unit, whereas for reactions 4 and 5 there are three ways (in each case) to replace either one or two out of three oxygen atoms in the carbonate group. Thus, entropic effects are also likely to favour both CO_2F and CaF_2 defect substitution over Ca-site substitution or FO_3 defects. Furthermore, the configurational entropies associated with CO_2F and CaF_2 substitutions are
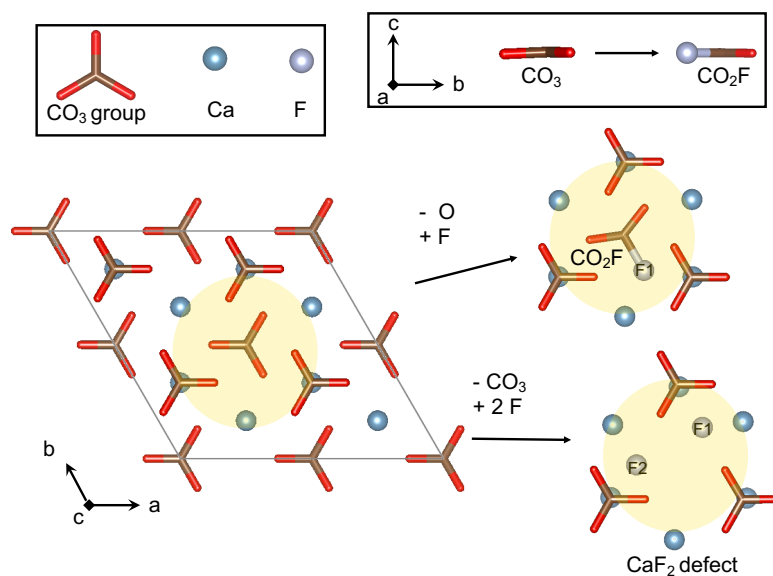
Figure 1: Minimum energy structure of calcite, with an indication of the local structure around a fluorine-bearing defect at the position indicated by the yellow shading for the CO_2F and CaF_2 substitutions. The solid lines around the structure mark the bounds of the simulation box.

expected to be similar.

3.2. Structural distortion

The incorporation of fluorine into each of the calcium carbonate polymorphs induces local structural distortion in the lattice around the incorporated atoms to some extent, breaking down the local symmetry of the host structures (Figures 1,2, and 3). The symmetries of the resultant structures have been analysed and are summarised in Table 2. It is found that they are $C2$ for CO_2F-bearing calcite, Pm for the CO_2F-bearing aragonite, which is the same as was found for iodine-substituted aragonite by Feng & Redfern (2018), and $P1$ for CO_2F-bearing vaterite. It should be stressed that we are not suggesting that halogen substitution at the ppm level, as seen in nature, would result in reduction of
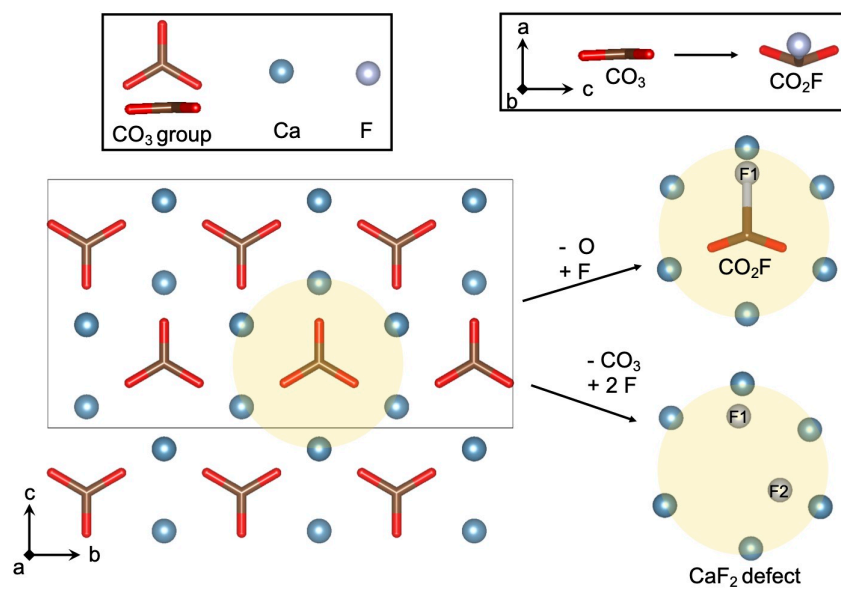
11

Figure 2: Minimum energy structure of aragonite, with an indication of the local structure around a fluorine-bearing defect at the position indicated by the yellow shading for the CO_2F and CaF_2 substitutions. The solid lines around the structure mark the bounds of the simulation box.
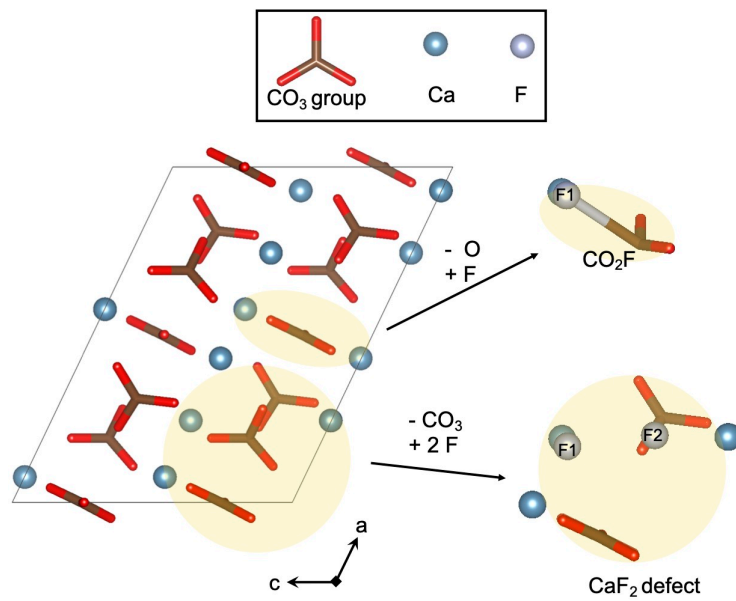
Figure 3: Minimum energy structure of calcite, with an indication of the local structure around a fluorine-bearing defect at the position indicated by the yellow shadings for the CO_2F and CaF_2 substitutions. The solid lines around the structure mark the bounds of the simulation box.

Table 2: Analysis of the structural distortions of CaCO$_3$ phases arising from incorporation of a CO$_2$F defect, with a comparison to those of the CaF$_2$ - defect type incorporation and of pure calcium carbonates.

Phase	Space group	Volume (Å^3)	Bond length (Å)		
			C-F	C-O$_{CO_2F}$	C-O$_{CO_3}$
CO$_2$F-bearing calcite	$C2$	366.3	2.08	1.26	1.29-1.30
CaF$_2$-bearing calcite	$C2$	381.4	-	-	
calcite	$R\bar{3}c$	381.5	-	-	
CO$_2$F-bearing aragonite	Pm	223.0	2.08	1.26	1.29-1.30
CaF$_2$-bearing aragonite	$P1$	233.6	-	-	
aragonite	$Pnma$	233.5	-	-	
CO$_2$F-bearing vaterite	$P1$	745.8	2.58	1.25	1.28-1.31
CaF$_2$-bearing vaterite	$P1$	775.8	-	-	
vaterite	Cc	782.4	-	-	

the long-range space group symmetry of a carbonate host crystal to these symmetries. Rather, these represent the symmetry of the local distortion that is to be expected around a halogen substituent atom when hosted within the matrix of such a phase. It appears that, in order to accommodate fluorine atoms by substitution of (CO$_3$)$^{2-}$ by (CO$_2$F)$^-$, the lattice becomes slightly smaller, with a small reduction in molar volume. The volumes of CO$_2$F-bearing and CaF$_2$-bearing carbonate unit cells are give in Table 2 from which it can be seen that the incorporation of fluorine by the CaF$_2$-type defect occurs with almost no change in density, or unit cell volume, in the case of calcite and aragonite, with the two F$^-$ anions that replace the CO$_3^{2-}$ group taking up almost identical space in the carbonate site position.

4. DISCUSSION

4.1. Structural incorporation

Experimental observations suggest that fluorine is not simply adsorbed onto calcium carbonate surfaces, but instead is incorporated into the CaCO$_3$ crystal

14

²⁷³ structure (Carpenter, 1969). Ichikuni (1979) carried out further studies of the

²⁷⁴ uptake of F^- in aragonite which indicated that fluorine is associated with struc-

²⁷⁵ tural incorporation into aragonite and suggested that one $(CO_3)^{2-}$ is replaced

²⁷⁶ by two F^- ions, co-precipitating with Ca^{2+} to form CaF_2.

²⁷⁷ Approximately half of the fluorine in seawater occurs in the form of molecular

²⁷⁸ complexes, principally as MgF^+ ion pairs. For the remainder, fluorine, due

²⁷⁹ to its high electronegativity, occurs as free anions (F^-). Clearly one possible

²⁸⁰ substitution mechanism corresponds to that in which one CO_3^{2-} oxy-anion in

²⁸¹ calcium carbonate is replaced by two F^- ions, as suggested earlier by Ichikuni

²⁸² (1979). Here, we have also explored other possible incorporation mechanisms.

²⁸³ We rule out co-precipitating with Ca^{2+} to nucleate and grow discrete crystalline

²⁸⁴ precipitates of CaF_2 since fluorite (CaF_2) is undersaturated in seawater and such

²⁸⁵ a complex is unlikely to precipitate (Sillén, 1961). Secondly, the structure of

²⁸⁶ fluorite is very different from that of the calcium carbonate polymorphs, and

²⁸⁷ the mismatch in structure means that the interface energy of any precipitate

²⁸⁸ would be high, such that nucleation and growth of precipitates of fluorite would

²⁸⁹ be inhibited. Furthermore, Ichikuni (1979) reported that fluoride in aragonites

²⁹⁰ precipitated from controlled aqueous solutions was homogeneously distributed,

²⁹¹ with no indication of discrete fluorite precipitates.

²⁹² In all three polymorphs (calcite, aragonite and vaterite), when we compare

²⁹³ a single atom of fluorine substituting onto the Ca-site, C-site or O-site, we

²⁹⁴ find that substitution of fluorine for oxygen (forming a $(CO_2F)^-$ complex) is

²⁹⁵ the most favoured. This is in contrast to the behaviour of iodine, which favours

²⁹⁶ substitution onto the C-site to form an iodate molecule in terms of incorporation

²⁹⁷ mechanism (Feng & Redfern, 2018). The formation of $(CO_2F)^-$ groups within

²⁹⁸ carbonate is not entirely surprising, in view of the earlier work of Bhargava &

²⁹⁹ Balasubramanian (2007). It was found that, in reaction between fluorine and

³⁰⁰ carbon dioxide, fluorine anions react with CO_2 to form $(CO_2F)^-$ groups, with

³⁰¹ one consequence of this reaction being the distortion of the CO_2 molecule away

³⁰² from linearity (Bhargava & Balasubramanian, 2007). We find a similar molec-

³⁰³ ular configuration in our simulations of carbonates adopting this substitution

mechanism. By extending the extent of substitution from one fluorine replacing oxygen at the carbonate group, to two fluorines replacing two carbonate oxygens and removal of the remaining oxygen and carbon atoms (the mechanism proposed by Ichikuni (1979) for aragonite) we arrive at an even more favoured fluorine incorporation mechanism. Not only does this process result in twice the amount of fluorine incorporated per defect, the energetics of the substitution reaction, reaction 5, are significantly smaller than the other mechanisms that we investigated.

Our simulations demonstrate that there are significant differences between the defect energies of the fluorine-bearing carbonate polymorphs. We find that the energy associated with incorporation of fluorine into calcite is the greatest of the three polymorphs, with incorporation of fluorine into aragonite and vaterite being much more favourable (Table 1). We note that our discussion is focussed entirely on thermodynamic considerations. For biogenic carbonates, non-equilibrium effects, such as those associated with cell metabolism, may also play significant roles in element incorporation. However, as discussed below, our results, based purely on the ground state thermodynamic properties of these structures, are reflected in observations of geochemical trends in natural systems, underlining the importance of equilibrium as a baseline consideration.

We conclude that fluorine will partition much more strongly into aragonite than into calcite. Comparing incorporation of fluorine into the three naturally-occurring polymorphs of calcium carbonate (including the metastable vaterite polymorph) we find that fluorine is expected to enter each polymorph with relative concentrations in the the order of vaterite $\gtrsim$ aragonite $\gg$ calcite. This finding is in agreement with the observations (on natural samples) of Carpenter (1969) who found that aragonites show much higher fluorine concentrations than calcites. The relative ease with which vaterite accommodates both the CO_2F and the CaF_2 defect does, however, raise the possibility of biogenic incorporation of fluorine into calcite via inheritance from a vaterite precursor. We note, for example, that Jacob et al. (2017) proposed that foraminiferal calcite forms via precursor vaterite, in the early stages of calcification. Given this, one might

16

expect that the stable "daughter" calcite forming the organism's shell may well reflect the partitioning, under biological calcification, set by that of the parent vaterite crystals.

4.2. Insights into ocean chemistry

The evidence of the uptake of fluorine by calcium carbonate is clear, and we have identified the likely mechanism of uptake. The earlier observations that aragonite is able to accommodate fluorine much more easily than calcite are born out in our results. Furthermore, the ion exchange reaction outlined in equation 1 is indeed confirmed as the most favourable route to incorporation. As a consequence, our results lend further support to the idea that the fluorine content of biogenic carbonates may be employed as a good indicator of the partial pressure of CO_2 (pCO_2) in the oceans, and hence of the impacts of changes in atmospheric carbon dioxide. Since equation 1 (equivalent to reaction 5 in our schemes) is an exchange reaction, it implies that fluorine in carbonate will have sensitivity to pCO_2, since increases in pCO_2 will result in reductions in pH and carbonate ion concentration ($[CO_3^{2-}]$) in seawater, which should result in an increase in fluorine concentration, measured in biogenic carbonates as F/Ca, in agreement with the results of Roepert et al. (2019). While we can expect this to be the dominant control on fluorine contents in biogenic calcium carbonates in the oceans, especially given this reaction incorporates two fluorine atoms into the structure, we also note that reaction 4, which is only slightly more exothermic, implies F in carbonate should have some sensitivity to pO_2 in seawater. This would imply an expected correlation between iodine (a redox-sensitive geochemical tracer in biogenic carbonates) and fluorine in carbonates.

5. CONCLUSIONS

The incorporation of fluorine into all three naturally-occurring polymorphs of calcium carbonate – calcite, aragonite and vaterite, has been investigated via first-principles computational methods. In each case the incorporation of a

17

fluorine atom is favoured most strongly as substituent of two fluorine ions for a carbonate, forming a CaF_2 defect. However, substitution of one fluorine for one oxygen in the form of $(CO_2F)^-$ groups, which causes local distortions of the structure over a length scale of around 10 Å, is also relatively easy, although not favoured to the extent of the CaF_2 defect. The incorporation of fluorine into vaterite is easiest, for all substitution mechanisms, although only marginally so for the CaF_2 and $(CO_2F)^-$ defects compared with incorporation into aragonite. Both aragonite and vaterite can, however, accommodated fluorine much more easily than the expected uptake of fluorine into calcite. These findings are supported by the experimentally observed trends in the distribution coefficients for fluorine into $CaCO_3$, which are larger for aragonite than for calcite. They are also consistent with the earlier experimental observations of fluorine incorporation into aragonite, lending further support to the idea that F/Ca, especially in biogenic aragonite (e.g. corals), can be used as a reliable proxy for ocean pCO_2, providing a further route for measurement of past changes in atmospheric CO_2 and associated paleoclimatic variations.

DATA AVAILABILITY

Research Data associated with this article can be access at:

Figshare https://doi.org/10.6084/m9.figshare.11858160.v1

AUTHOR CONTRIBUTIONS

XF, ZS and SATR initialised the idea of this study during conversations over coffee in the common room of the Department of Earth Sciences, Downing Street, Cambridge. XF conducted the calculations and interpreted the data. XF, ZS and SATR analysed results and wrote the manuscript together.

COMPETING INTERESTS

The authors declare no competing interests.

ACKNOWLEDGEMENT

References

Archer, T., Birse, S., Dove, M., Redfern, S., Gale, J., & Cygan, R. (2003). An interatomic potential model for carbonates allowing for polarization effects. *Physics and Chemistry of Minerals*, *30*. doi:`10.1007/s00269-002-0269-z`.

Bhargava, B., & Balasubramanian, S. (2007). Probing anion–carbon dioxide interactions in room temperature ionic liquids: Gas phase cluster calculations. *Chemical Physics Letters*, *444*, 242 – 246. URL: `http://www.sciencedirect.com/science/article/pii/S0009261407009803`. doi:`https://doi.org/10.1016/j.cplett.2007.07.051`.

Carpenter, R. (1969). Factors controlling the marine geochemistry of fluorine. *Geochimica et Cosmochimica Acta*, *33*, 1153–1167. URL: `https://linkinghub.elsevier.com/retrieve/pii/0016703769900386`. doi:`10.1016/0016-7037(69)90038-6`.

De Villiers, J. P. R. (1971). Crystal structures of aragonite , strontianite , and witherite. *The American Mineralogist*, *56*, 758–767.

Demichelis, R., Raiteri, P., Gale, J. D., & Dovesi, R. (2013). Examining the accuracy of density functional theory for predicting the thermodynamics of water incorporation into minerals: The hydrates of calcium carbonate. *Journal of Physical Chemistry C*, *117*, 17814–17823. doi:`10.1021/jp4048105`.

Feng, X., & Redfern, S. (2018). Iodate in calcite, aragonite and vaterite CaCO3: Insights from first-principles calculations and implications for the I/Ca geochemical proxy. *Geochimica et Cosmochimica*

Acta, . URL: https://www.sciencedirect.com/science/article/pii/S0016703718300875. doi:10.1016/J.GCA.2018.02.017.

Graf, D. L. (1961). Crystallographic tables for the rhombohedral carbonates. *American Mineralogist*, *46*, 1283–1316.

Green, M. A., & Aller, R. C. (2001). Early diagenesis of calcium carbonate in Long Island Sound sediments: Benthic fluxes of Ca2+ and minor elements during seasonal periods of net dissolution. *Journal of Marine Research*, *59*, 769–794. URL: http://www.ingentaselect.com/rpsv/cgi-bin/cgi?ini=xref{&}body=linker{&}reqdoi=10.1357/002224001762674935. doi:10.1357/002224001762674935.

Ichikuni, M. (1979). Uptake of fluoride by aragonite. *Chemical Geology*, *27*, 207–214. URL: https://linkinghub.elsevier.com/retrieve/pii/0009254179900391. doi:10.1016/0009-2541(79)90039-1.

Jacob, D. E., Wirth, R., Agbaje, O. B., Branson, O., & Eggins, S. M. (2017). Planktic foraminifera form their shells via metastable carbonate phases. *Nature Communications*, *8*. doi:10.1038/s41467-017-00955-0.

Kendrick, M. A. (2018). Halogens in seawater, marine sediments and the altered oceanic lithosphere. In *The role of halogens in terrestrial and extraterrestrial geochemical processes* (pp. 591–648). Springer.

Kitano, Y., & Okumura, M. (1973). Coprecipitation of fluoride with calcium carbonate. *Geochemical Journal*, *7*, 37–49.

Kresse, G., & Furthmüller, J. (1996). Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B*, *54*, 11169–11186. URL: https://link.aps.org/doi/10.1103/PhysRevB.54.11169. doi:10.1103/PhysRevB.54.11169. arXiv:0927-0256(96)00008.

Momma, K., & Izumi, F. (2011). Vesta 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of applied crystallography*, *44*, 1272–1276.

Ohde, S., & Kitano, Y. (1980). Incorporation of fluoride into Ca-Mg carbonate. *Geochemical Journal*, *14*, 321–324. URL: `http://joi.jlc.jst.go.jp/JST.Journalarchive/geochemj1966/14.321?from=CrossRef`. doi:`10.2343/geochemj.14.321`.

Opdyke, B. N., Walter, L. M., & Huston, T. J. (1993). Fluoride content of foraminiferal calcite: Relations to life habitat, oxygen isotope composition, and minor element chemistry. *Geology*, *21*, 169. URL: `https://pubs.geoscienceworld.org/geology/article/21/2/169-172/186463`. doi:`10.1130/0091-7613(1993)021<0169:FCOFCR>2.3.CO;2`.

Perdew, J. J. P., Burke, K., & Ernzerhof, M. (1996). Generalized Gradient Approximation Made Simple. *Physical Review Letters*, *77*, 3865–3868. URL: `https://link.aps.org/doi/10.1103/PhysRevLett.77.3865`. doi:`10.1103/PhysRevLett.77.3865`. arXiv:`0927-0256(96)00008`.

Perdew, J. P., Chevary, J. A., Vosko, S. H., Jackson, K. A., Pederson, M. R., Singh, D. J., & Fiolhais, C. (1992). Applications of the generalized gradient approximation for exchange and correlation. *Phys Rev B*, *46*, 6671–6687. doi:`10.1103/PhysRevB.46.6671`.

Podder, J., Lin, J., Sun, W., Botis, S. M., Tse, J., Chen, N., Hu, Y., Li, D., Seaman, J., & Pan, Y. (2017). Iodate in calcite and vaterite: Insights from synchrotron X-ray absorption spectroscopy and first-principles calculations. *Geochimica et Cosmochimica Acta*, *198*, 218–228. doi:`10.1016/j.gca.2016.11.032`.

Ramos, A. A., Ohde, S., Hossain, M. M. M., Ozaki, H., Sirirattanachai, S., & Apurado, J. L. (2005). Determination of fluorine in coral skeletons by instrumental neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry*, *266*, 19–29. URL: `http://link.springer.com/10.1007/s10967-005-0863-x`. doi:`10.1007/s10967-005-0863-x`.

Roepert, A., Polerecky, L., Geerken, E., Reichart, G.-J., & Middelburg, J. J. (2019). Distribution of chlorine and fluorine in benthic foraminifera. *Biogeosciences Discussions*, *2019*, 1–27. URL: `https://www.biogeosciences-discuss.net/bg-2019-424/`. doi:`10.5194/bg-2019-424`.

Rosenthal, Y., & Boyle, E. A. (1993). Factors controlling the fluoride content of planktonic foraminifera: An evaluation of its paleoceanographic applicability. *Geochimica et Cosmochimica Acta*, *57*, 335–346. URL: `https://linkinghub.elsevier.com/retrieve/pii/001670379390435Y`. doi:`10.1016/0016-7037(93)90435-Y`.

Rosenthal, Y., Boyle, E. A., & Slowey, N. (1997). Temperature control on the incorporation of magnesium, strontium, fluorine, and cadmium into benthic foraminiferal shells from Little Bahama Bank: Prospects for thermocline paleoceanography. *Geochimica et Cosmochimica Acta*, *61*, 3633–3643. URL: `https://linkinghub.elsevier.com/retrieve/pii/S0016703797001816`. doi:`10.1016/S0016-7037(97)00181-6`.

Rude, P. D., & Aller, R. C. (1991). Fluorine mobility during early diagenesis of carbonate sediment: An indicator of mineral transformations. *Geochimica et Cosmochimica Acta*, *55*, 2491–2509. URL: `https://linkinghub.elsevier.com/retrieve/pii/001670379190368F`. doi:`10.1016/0016-7037(91)90368-F`.

Sillén, L. G. (1961). The physical chemistry of seawater. *Oceanography*, .

Steiner, Z., Erez, J., Shemesh, A., Yam, R., Katz, A., & Lazar, B. (2014). Basin-scale estimates of pelagic and coral reef calcification in the Red Sea and Western Indian Ocean. *Proceedings of the National Academy of Sciences*, *111*, 16303–16308. URL: `http://www.pnas.org/lookup/doi/10.1073/pnas.1414323111`. doi:`10.1073/pnas.1414323111`.

Steiner, Z., Turchyn, A. V., Harpaz, E., & Silverman, J. (2018). Water chemistry reveals a significant decline in coral calcification rates in the southern

Red Sea. *Nature Communications*, *9*, 3615. URL: http://www.nature.com/articles/s41467-018-06030-6. doi:10.1038/s41467-018-06030-6.

Tanaka, K., & Ohde, S. (2010). Fluoride in coral aragonite related to seawater carbonate. *Geochemical Journal*, *44*, 371–378. URL: http://jlc.jst.go.jp/DN/JST.JSTAGE/geochemj/1.0079?lang=en{&}from=CrossRef{&}type=abstract. doi:10.2343/geochemj.1.0079.

Tanaka, K., Ono, T., Fujioka, Y., & Ohde, S. (2013). Fluoride in non-symbiotic coral associated with seawater carbonate. *Marine Chemistry*, *149*, 45–50. URL: https://linkinghub.elsevier.com/retrieve/pii/S0304420312001399. doi:10.1016/j.marchem.2012.12.004.