



Iodate in calcite, aragonite and vaterite CaCO_3 : Insights from first-principles calculations and implications for the I/Ca geochemical proxy

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Abstract

The incorporation of iodine into each of the three polymorphs of CaCO_3 – calcite, aragonite and vaterite, is compared using first-principles computational simulation. In each case iodine is most easily accommodated as iodate (IO_3^-) onto the carbonate site. Local strain fields around the iodate solute atom are revealed in the pair distribution functions for the relaxed structures, which indicate that aragonite displays the greatest degree of local structural distortion while vaterite is relatively unaffected. The energy penalty for iodate incorporation is least significant in vaterite, and greatest in aragonite, with the implication that iodine will display significant partitioning between calcium carbonate polymorphs in the order vaterite > calcite > aragonite. Furthermore, we find that trace iodine incorporation into vaterite confers improved mechanical strength to vaterite crystals. Our results support the supposition that iodine is incorporated as iodate within biogenic carbonates, important in the application of I/Ca data in palaeoproxy studies of ocean oxygenation. Our observation that iodate is most easily accommodated into vaterite implies that the presence of vaterite in any biocalcification process, be it as an end-product or a precursor, should be taken into account when applying the I/Ca geochemical proxy.

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1. INTRODUCTION

Understanding seawater oxygen content is important, since oxygen minimum zones (OMZs) adversely affect marine fisheries and biological productivity. Oxygen depletion appears to be affecting a greater and greater volume of intermediate ocean waters, and has been associated with ocean warming and climate change (Keeling et al., 2010). Understanding the climate sensitivity of the oceans' oxygen minimum zone, both today and over geological time scales,

demands the development of a geochemical proxy for water oxygen content. As a redox-sensitive element, iodine has been proposed as a suitable proxy for this purpose. Iodine has been recognised as a promising geochemical indicator for oxygen content: the variation of speciation of iodine in seawater, as either iodide (I^-) or iodate (IO_3^-) anions, and the iodide/iodate redox potential lies close to that of $\text{O}_2/\text{H}_2\text{O}$ (Rue et al., 1997). As oxygen content decreases, the speciation of iodine in aqueous solutions changes from dominantly iodate to iodide, and iodide is thermodynamically stable in anoxic waters (Chapman and Truesdale, 2011). Iodine accumulates in planktonic and benthic marine calcifiers, and follows a nutrient-like vertical distribution in the oceans (Elderfield and Truesdale, 1980). Diagenetic processes may act as a further control on the presence of iodine

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in pore fluids (Kennedy and Elderfield, 1987). Since I^- does not enter carbonate minerals, while IO_3^- does, the iodine content of marine carbonates may be used as a proxy for seawater $[O_2]$. More generally, halogens play an important part in Earth's ecosystems, and volcanic emissions of halogens are known to be considerable, but most studies to date have focussed on chlorine and fluorine. Typical concentrations of iodine in carbonate rocks lie in the ppm range (Fuge and Johnson, 1986) and may range as high as 500 nM in ocean waters (Hardisty et al., 2017). The fates of iodine in the solid Earth, in crustal and mantle rocks and reservoirs, and its sources, sinks and fluxes, remain undefined and largely unknown, although the possible transfer of iodine into the mantle through subducted oceanic sediments remains a clear possibility.

Inorganic precipitation experiments have found that I/Ca ratios in calcites crystallised from solution are linearly-dependent upon the IO_3^- concentration of the parent water, but are independent of I^- content of such water (Lu et al., 2010). Lu et al. (2010) carried out experiments in which they grew synthetic calcites spiked with iodine in solution, either as iodide or iodate. While they found little dependence of the I/Ca ratios in their samples for the iodide-bearing solutions, they saw a linear relationship between I/Ca and iodate concentration and concluded that the likely substitution mechanism is IO_3^- substituting for the CO_3^{2-} oxy-anion in calcite: since IO_3^- occurs in oxygenated water, the I/Ca ratio was found to be higher in the test of foraminifera grown in high $[O_2]$ water. Their interest was in the application of measurements of iodine in calcite as a geochemical proxy for seawater redox potential, given the fact that iodate/iodide speciation changes with the oxidation state of seawater. This is particularly interesting because I/Ca in benthic foraminifera provide a route to measuring the variations in oxygen contents of bottom waters (Glock et al., 2014). Additionally, low I/Ca ratios in fossil planktonic foraminifera have been identified with ocean anoxia in the stagnant oceans of the mid-Cretaceous, associated also with organic-rich clay-bearing sediments (Zhou et al., 2015). In the same way that B, Mg and Na have been seen to vary through the test wall of a foraminifera (Branson et al., 2013; Branson et al., 2015; Redfern et al., 2017), so I/Ca ratios also display heterogeneity, in the basis of ICP-MS measurements (Glock et al., 2016). If such intra-test heterogeneities are indeed caused by variations in the redox-conditions over the lifetime of a single foraminiferal specimen, it may even be possible to reconstruct relative $[O_2]$ changes in bottom waters on sub-annual time scales, although the biological controls on iodine incorporation are unclear. These previous studies made no direct measurement, by spectroscopy or other structural means, of the speciation and incorporation state of the iodine in their samples, however. A fully quantitative relationship between dissolved oxygen and foraminiferal I/Ca has yet to be developed, and inferences from I/Ca remain qualitative. None the less, the fate of iodine in biogenic carbonates has been found to be a reliable indicator of ocean oxidation state, with results from foraminiferal calcite being employed to infer bathymetric variations in deoxygenation of ancient and modern oceans (Zhou et al., 2014; Lu et al., 2016), for example.

It is worth noting that further interest in the fate of iodine in the near surface solid Earth and in ground waters has arisen due to its prevalence in nuclear waste materials. Iodine has one stable isotope, ^{127}I , but twenty-five radioactive isotopes and ^{131}I is an acute radioactive contaminant. Due to its long half-life (1.6×10^7 yrs), high inventories in typical spent fuel, high bioactivity and high mobility, ^{129}I released into the environment has been identified as a major potential hazard in groundwater near nuclear waste disposal sites (Gephart, 2010; Kaplan et al., 2011; Kaplan et al., 2014). Understanding the interaction between iodine in aqueous solution and carbonate mineral precipitates in sediments (as well as in concrete repository structures) is crucial in understanding the pathways and risks from ^{129}I . Much of the ^{127}I and ^{129}I that originally existed as aqueous species in contaminated groundwater at the Hanford nuclear site co-precipitated into groundwater calcite, mainly as iodate (Zhang et al., 2013), demonstrating the important role in the geochemical immobilization of radioactive iodine played by the interaction between $CaCO_3$ and aqueous iodine species.

In order to better understand the incorporation of iodine into carbonates, it is necessary to first determine the ultimate location of iodine within carbonate mineral structures. Several early studies tackled the incorporation of trace and major elements into calcite but they mainly focused on exchange of Ca^{2+} with other cations, such as Mg^{2+} , Na^+ , Fe^{2+} , Zn^{2+} , As^{5+} , Sr^{2+} . More recently, attention has turned to anion substitutions into carbonates, building on earlier work characterizing sulfate incorporation into carbonate minerals (Takano et al., 1980). Electron paramagnetic resonance (EPR) spectroscopy and X-ray diffraction have been used to study the possible incorporation of SO_4^{2-} , NO_3^- and Cl^- into the calcite crystal structure and to find out the possible sites and mode of their incorporation (Kontrec et al., 2004). The results indicated that the calcite lattice becomes distorted due to the incorporation of such anions. Based on these studies, it was concluded that sulfate can be incorporated into the calcite lattice and substitute for carbonate ions. Their results were supported by a number of later experimental investigations (Takano et al., 1980; Fernández-Díaz et al., 2010; Balan et al., 2017). Extended X-ray absorption fluorescence spectroscopy (EXAFS) was also used to determine how the tetrahedral SeO_4^{2-} species are accommodated in the bulk calcite structure (Reeder et al., 1994; Lambie et al., 1995). Lambie et al. (1995) found that tetrahedral SeO_4^{2-} oxy-anions substitute for trigonal CO_3^{2-} in calcite. As far as iodine incorporation is concerned, an X-ray single crystal electron density study of calcite Maslen et al. (1993) attempted to infer the influence of dilute iodate incorporation and postulated that it substitutes for the carbonate ion in calcite based on the fact that the Ca–O distance in calcium iodate, $Ca(IO_3)_2$, is similar to that in calcite. Most recently, Podder et al. (2017) used a combination of X-ray absorption spectroscopy and first principles calculations to identify the nature of iodate in calcite and vaterite, confirming that this is the dominant incorporation mode.

Here, we extend our understanding of the incorporation of iodine in calcium carbonates using *ab initio* computa-

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