Halogen incorporation into calcite, aragonite and vaterite $CaCO_3$: Computational chemistry insights and geochemistry implications

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The abundant occurrence of calcium carbonate minerals in marine sediments and their high fluorine content suggests that fluorine is a good candidate for re-constructing paleoceanographic parameters. However, the potential of fluorine as a palaeoproxy had hardly been explored, and fundamental insights into the behaviour of fluorine in biogenic carbonates and marine sediments is required. We have used a first-principles modelling approach to analyse the incorporation mechanisms of fluorine into crystalline calcium carbonates. We find that F is incorporated into the CaCO3 lattice, replacing one oxygen atom within the carbonate group to form a $(CO_2F)^-$ group. Our simulations also suggest that fluorine is preferentially incorporated into all the three naturally-occurring polymorphs of calcium carbonate in the order of aragonite > vaterite > calcite, and that the effect of incorporation is to increase the density, or decrease the molar volume of the carbonate, suggesting that pressure may amplify fluorine incorporation.

In contrast, iodine is most easily accommodated as iodate (IO_3^-) onto the carbonate site. Local strain fields around the iodate solute atom indicate that aragonite displays the greatest degree of local structural distortion while vaterite is relatively unaffected. The energy penalty for iodate incorporation indicates that iodine will display significant partitioning between calcium carbonate polymorphs in the order vaterite > calcite > aragonite. 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.