Isotopic fractionation accompanying CO₂ hydroxylation and carbonate precipitation from high pH waters at The Cedars, California, USA

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Abstract

The Cedars ultramafic block hosts alkaline springs (pH > 11) in which calcium carbonate forms upon uptake of atmospheric CO₂ and at times via mixing with surface water. These processes lead to distinct carbonate morphologies with “floes” forming at the atmosphere-water interface, “snow” of fine particles accumulating at the bottom of pools and terraced constructions of travertine. Floe material is mainly composed of aragonite needles despite CaCO₃ precipitation occurring in waters with low Mg/Ca (<0.01). Precipitation of aragonite is likely promoted by the high pH (11.5–12.0) of pool waters, in agreement with published experiments illustrating the effect of pH on calcium carbonate polymorph selection.

The calcium carbonates exhibit an extreme range and approximately 1:1 covariation in δ¹³C (‰ to/Co) and δ¹⁸O (‰ to/Co) that is characteristic of travertine formed in high pH waters. The large isotopic fractionations have previously been attributed to kinetic isotope effects accompanying CO₂ hydroxylation but the controls on the δ¹³C-δ¹⁸O end-members and slope have not been fully resolved, limiting the use of travertine as a paleoenvironmental archive. The limited areal extent of the springs (∼0.5 km²) and the limited range of water sources and temperatures, combined with our sampling strategy, allow us to place tight constraints on the processes involved in generating the systematic C and O isotope variations.

We develop an isotopic reaction–diffusion model and an isotopic box model for a CO₂-fed solution that tracks the isotopic composition of each dissolved inorganic carbon (DIC) species and CaCO₃. The box model includes four sources or sinks of DIC (atmospheric CO₂, high pH spring water, fresh creek water, and CaCO₃ precipitation). Model parameters are informed by new floe Δ⁴⁴Ca data (−0.75 ± 0.07‰), direct mineral growth rate measurements (4.8 to 10⁻⁷ mol/m²/s) and by previously published elemental and isotopic data of local water and DIC sources. Model results suggest two processes control the extremes of the array: (1) the isotopically light end member is controlled by the isotopic composition of atmospheric CO₂ and the kinetic isotope fractionation factor (KFF (‰) = (α − 1) × 1000) accompanying CO₂ hydroxylation, estimated here to be −17.1 ± 0.8‰ (vs. CO₂(aq)) for carbon and −7.1 ± 1.1‰ (vs. ‘CO₂(aq) + H₂O’) for oxygen at 17.4 ± 1.0 °C. Combining our results with revised CO₂ hydroxylation KFF values based on previous work suggests consistent KFF values of −17.0 ± 0.3‰ (vs. CO₂(aq)) for carbon and −6.8 ± 0.8‰ for oxygen (vs. ‘CO₂(aq) + H₂O’) over the 17–28 °C temperature range.
range. (2) The isotopically heavy endmember of calcium carbonates at The Cedars reflects the composition of isotopically equilibrated DIC from creek or surface water (mostly HCO₃⁻, pH = 7.5–8.7) that occasionally mixes with the high-pH spring water. The bulk carbonate δ¹³C and δ¹⁸O values of modern and ancient travertines therefore reflect the proportion of calcium carbonate formed by processes (1) and (2), with process (2) dominating the carbonate precipitation budget at The Cedars. These results show that recent advances in understanding kinetic isotope effects allow us to model complicated but common natural processes, and suggest ancient travertine may be used to retrieve past meteoric water δ¹⁸O and atmospheric δ¹³C values. There is evidence that older travertine at The Cedars recorded atmospheric δ¹³C that predates large-scale combustion of fossil fuels.

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1. INTRODUCTION

Most Earth-surface carbonate minerals precipitate out of stable isotope equilibrium with their host aqueous solution (Coplen, 2007; Watkins et al., 2013, 2014; Deviendrt et al., 2017; Daëron et al., 2019). Deviations from isotope equilibrium are manifested in a variety of ways. One of the most striking ways, still not fully understood, is a strong correlation between δ¹³C and δ¹⁸O in carbonates precipitated under different circumstances, from marine calcifying organisms (e.g., McConnaughey, 1989; Spero et al., 1997; Adkins et al., 2003; Kimball et al., 2014; Hermoso et al., 2014; Chen et al., 2018) to cryogenic calcium carbonates (Clark and Lauriol, 1992; Zák et al., 2008), lacustrine carbonates (Talbot, 1990), and speleothem carbonates formed by CO₂ degassing (Daëron et al., 2011; Tremaine et al., 2011). The slope of the δ¹³C-δ¹⁸O covariation varies because kinetic isotope effects in the CaCO₃-DIC-H₂O system are sensitive to factors such as temperature, solution pH, mixing between DIC reservoirs, the residence time of DIC in solution, whether CO₂ is ingassing or outgassing from solution, and whether the system is open versus closed (e.g., McConnaughey, 1989; Clark et al., 1992; Falk et al., 2016; Deviendrt et al., 2017; Chen et al., 2018).

Calcium carbonates formed in hyperalkaline springs exhibit some of the largest and most systematic variations in δ¹³C and δ¹⁸O (O’Neil and Barnes, 1971; Clark and Fontes, 1990; Clark et al., 1992; Meister et al., 2011; Leleu et al., 2016; Falk et al., 2016). The archetype locality is a set of carbonate formations precipitating from springs emanating from serpentinized peridotite in the Samail ophiolite, Sultanate of Oman (Barnes et al., 1978; Clark et al., 1992; Kelemen et al., 2011; Mervine et al., 2014; Falk et al., 2016). Fig. 1 (data from Clark and Fontes, 1990; Clark et al., 1992; Falk et al., 2016; Mervine et al., 2014) shows the strong δ¹³C-δ¹⁸O correlation spanning a range of about 25‰ in both ¹³C and ¹⁸O, with most of the values being isotopically lighter than the expected equilibrium values. The isotopically light endmember of the δ¹³C-δ¹⁸O array has been attributed to hydroxylation of dissolved CO₂ ingassing from the atmosphere (Clark et al., 1992). The rest of the array has been attributed to some combination of mixing between different DIC sources, partial equilibration of DIC, and post-depositional recrystallization (Falk et al., 2016). Recent developments of numerical models that quantify kinetic isotope effects in the CaCO₃-DIC-H₂O system (Deviendrt et al., 2017; Sade and Halevy, 2017; Chen et al., 2018) provide an opportunity to gain a quantitative understanding of the peculiar and large kinetic isotope effects in high pH environments.

The calcium carbonate samples from Oman represented in Fig. 1 were collected over an area of 50 × 200 km from calcium-hydroxide springs (pH = 11.2–12.1) spanning a large range in temperature (22–32 °C), in δ¹³C of DIC surface and ground waters, and in the age of samples (0–40 ka). This explains the large range of possible equilibrium calcite values (Fig. 1). In this study, we investigate a similar high-pH system, The Cedars, where the springs are within a 0.5 km² area, the spring waters have a more constant temperature (17.4 ± 1.0 °C) and δ¹³C value. Our approach is to determine the calcite and aragonite growth rates using Ca isotopes and detailed field observations to evaluate calcium carbonate δ¹³C and δ¹⁸O values in the context of these mineral growth rate data, solution chemistry, travertine forms, and carbon sources/transport.

Fig. 1. δ¹³C vs. δ¹⁸O of carbonates associated with high pH springs in Oman emanating from ultramafic rocks of the Samail ophiolite.
2. THE CEDARS

The Cedars (aka Cazadero; Barnes et al. 1967) peridotite is a relatively small tectonically emplaced fault-bounded wedge of ultramafic rock located in the California Coast Range north of San Francisco (Coleman 2000; Blake et al., 2012; Fig. 2). The dominant rock type is harzburgite with lesser amounts of dunite. This fragment of Jurassic age oceanic lithosphere has been inferred to be an obducted abyssal peridotite from an oceanic fracture zone (Coleman 2000), or alternatively as the basal peridotite of the Coast Range Ophiolite formed in the mantle wedge above the Mesozoic California-margin subduction zone (Choi et al. 2008). The central portion of The Cedars is partially serpentinized while the margins consist of sheared serpentinite (Blake et al. 2012). The Cedars ultramafic body is in fault contact with Franciscan Complex mélange greywacke and shale (Coleman 2000). It has a dipping, wedge-shaped structural geometry, extending to a depth of 4 km but with an average thickness of 2 km or less (Blake et al. 2002).

A series of springs emerge along the course of Austin Creek at the bottom of the main canyon between ~275 m and 335 m elevation. Some springs produce pools and terraced deposits adjacent to the creek before emptying into the creek. At other locations springs enter the creek directly from the bottom. An example at the Barnes Spring Complex (BSC, Fig. 2) of a spring-fed pool adjacent to Austin Creek is shown in Fig. 3. The unusual nature of the springs at The Cedars was first recognized and described by Barnes et al. (1967) and Barnes and O’Neil (1969). They found that the springs produce ultrabasic waters (pH = 11.7) with low DIC, Mg, Fe, and silica concentrations but a relatively high Ca concentration. They attribute the spring water’s unusual chemical characteristics to on-going serpentinization of primary ultramafic rock at shallow depth. Isotope studies demonstrated that the spring waters have a meteoric origin as opposed to an ancient connate origin from the underlying Franciscan formation (Barnes and O’Neil, 1969; Barnes et al. 1978), and that calcium carbonates precipitating from the ultrabasic waters have unusually low δ13C and δ18O values (O’Neil and Barnes, 1971).

Morrill et al. (2013) conducted a more extensive study of the high pH waters of The Cedars. They identified two types of ultrabasic water that variably mix: (1) waters with deep flow paths that interacted with the underlying Franciscan Complex enriching the waters in K⁺, other salts and volatile organic compounds before encountering ultramafic rock, and (2) waters with shallow paths that pass solely through ultramafic rock and are characterized by lower salinity and [K⁺]. The springs exhibit stable temperatures with time and season (spring vs. fall), averaging 17 ± 1°C (Morrill et al., 2013; Suzuki et al., 2013). Tritium dating of water samples by Suzuki et al. (2017) indicates that water with deep flow paths, as at the Grotto Pool Springs, has an age greater than 60 years (<0.8 Tritium units, TU), while

Fig. 2. Maps showing the location of The Cedars and sampling locations (modified after Morrill et al. 2013). Using the nomenclature of Morrill et al. (2013), BSC = Barnes Spring Complex, GPS = Grotto Pool Springs. The Wedding Cake is at the NS1 locality above Mineral Falls.
Barnes Complex spring water, with an inferred shallow flow path, gave a value of 2.3 TU, possibly indicating an age younger than 10 years since that value is similar to contemporaneous Bay Area precipitation (1.3–2.2 TU, Harms 2015).

3. METHODS

3.1. Sampling

Samples were collected on eight visits to The Cedars in 2013, 2014, 2016 and 2018. Four sites were sampled (Fig. 2): (1) The Wedding Cake above Mineral Falls, (2) The Barnes Spring Complex (BSC), (3) Grotto Pool Springs (GPS), and (4) “New” Pool within Austin Creek ∼ 250 m upstream of BSC. Water samples from the high pH springs and from Austin Creek were filtered to 0.22 μm using Durapore filter units (Millipore), collected in HDPE bottles and acidified to pH 2 using high purity HNO₃ (Baseline Nitric Acid, Seastar Chemicals). Prior to collection, the pH of the sampling source was measured with an Orion hand-held pH meter (Thermo Scientific). Samples of calcium carbonate collected are of several types as illustrated in Fig. 3: (1) partially consolidated material from rims of pools; (2) precipitates from the surfaces of pools (called here floes); (3) dendritic forms and encrustations from sites of creek-spring mixing; (4) unconsolidated material (called here snow) from pool bottoms; and (5) solid, old travertine deposits. Surface floes were either skimmed from the surface or captured on screens.

3.2. Analytical Methods

Below are brief descriptions of the analytical techniques used in this study. Further details are provided in Supplementary material.

Samples of calcium carbonate and water were analyzed for calcium isotope composition using thermal ionization mass spectrometry on a Triton (ThermoFisher) multicollector instrument. Prior to chemical separation, samples were spiked with a ⁴²Ca-⁴⁸Ca double spike. The Ca isotope results (δ⁴⁴Ca) are reported as per mil deviations of the ⁴⁴Ca/⁴⁰Ca ratio from Bulk Silicate Earth (BSE; Nielsen et al. 2011). Our measurements confirm the BSE reference ⁴⁴Ca/⁴⁰Ca ratio is 0.96 ± 0.05‰ higher than the value for SRM915a.

Oxygen and carbon isotope analyses of carbonate samples were conducted in the Center for Stable Isotope Biogeochemistry (CSIB), Department of Integrative Biology, University of California, Berkeley, using a GV IsoPrime mass spectrometer equipped with Dual-Inlet and Multi-Carb systems. Results are reported relative to Vienna Pee Dee Belemnite (VPDB). The overall external analytical precision is ±0.05‰ for δ¹³C and ±0.07‰ for δ¹⁸O.

Elemental concentrations of the water samples were determined by Quadrupole-ICPMS (Elan DRC II, PerkinElmer SCIEX, USA). Images of calcium carbonate samples were obtained with a Zeiss EVO-LS10® scanning electron microscope (SEM), with capabilities of secondary electron (SE) imaging and back-scattered electron (BSE) imaging. Phase identification and quantification in selected solid samples were carried out via X-Ray powder diffra-
tion (XRPD) with a Rigaku SmartLab® X-ray diffractometer.

4. RESULTS

4.1. XRPD and SEM observations

Fourteen carbonate samples were selected for XRPD analysis to cover the observed range in sample textures. The fractions of the identified mineral phases are given in Table 1. Aragonite and/or calcite are found in all samples, with aragonite ranging from 18% to 99.7%, and calcite ranging from 0.14% to 82%. Small amounts of vaterite (a polymorph of Ca carbonate) were identified in one floe sample (BSC Carb I: 0.5 ± 0.2%) and in one sample of a pool edge (BSC PE-C2 crust: 0.6 ± 0.2%). Brucite (Mg (OH)₂) was found in some samples of BSC pool edges (PB-C2 and PE-C2: 3 and 8%, respectively), in a filtered snow sample from BSC (PB-1: 68.0 ± 0.8%), a GPS pool (Carb K: 49.5%) and in one of the samples from mixed spring-creek water (Carb AA: 7.7%). In samples of snow filtered from GPS pool water, both hydromagnesite (Carb J: 27%; Carb K: 49.5%) and nitromagnesite (Carb J: 4.5%; Carb K: 2.3%) were detected. Nesquehonite (MgCO₃·H₂O) was also detected in one sample (Carb K: 3%).

SEM images of a sample taken from the rim of a pool (Carb A, Fig. S1) show elongate crystals up to 10–15 µm of aragonite (as identified by the XRPD analysis) gathered in bundles, sprays and spheres. The samples from the New Pool (Carb B and Carb C) affected by creek mixing, is also identified by XRPD as 100% aragonite, and consist of sharp needles up to at least 40 µm grouped in radial sprays or spheres (Fig. S2 and S3). Both the soft encrustation on rock and the elongate branching forms display similar micro-textures.

The samples of floes have a more varied mineralogy and texture than samples from the Wedding Cake and from the New Pool. Fig. 4 compares the inferred top (upwards from water) and bottom (down into the water) surfaces of floe carbonates from a BSC pool. The top-side of the floe (Fig. 4A) displays radiating horizontal sprays of aragonite crystals, forming a relatively flat surface. In contrast, the bottom side (Fig. 4B) is rougher, with the terminations of the aragonite sprays forming a hummocky surface. Calcite rhombohedra are scattered across this surface, apparently forming largely after growth of the aragonite sprays. Open areas constitute approximately 15–20% of the area of this floe sample (Carb D). Fig. S4 provides views of the broken edges of this floe material (Carb D). In the cross-sections the aragonite sprays can be seen to radiate from points, forming intersecting hemispheres. In this case the floe has a thickness of about 10 to 12 µm. Similar differences between the tops and bottoms of floes are confirmed by examination of carefully collected samples so that flakes of known original orientation could be examined by SEM (Fig. 4C).

The growth rate of the floes was determined by measuring the thickness as a function of time. After eight days of carbonate growth, floe thickness was 20–25 µm, as determined using SEM images of oriented fragments (Fig. 5).

<table>
<thead>
<tr>
<th>Table 1: XRPD results for mineral compositions of carbonate samples.</th>
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<td>PB-C2 crust</td>
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<td>PE-C2 crust</td>
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In the inset to Fig. 5, a piece of floe collected after four days of growth shown at the same scale has half the thickness of the eight-day growth, suggesting a constant linear growth rate of about 3 μm/day.

Fig. 4. SEM images of floe calcium carbonate from BSC pool surface. (A) Image of the inferred top side of the floe (Carb D). Texture consists of radiating crystals of aragonite (identified in XRPD) in a horizontal plane (detail in inset 1), showing in places a plumose/branching texture (inset 2). (B) The inferred bottomside of the floe. To right is an enlargement of the area in the dashed box in the left panel. Left image show calcite rhombs on sprays of aragonite crystals. In contrast to the side shown in A, this side is hummocky and less smooth. In this example, there are open areas between aragonite sprays representing approximately 10–15% of the area of the floe. (C) SEM image comparing the top and bottom sides of an another example of floe carbonate (flakes were placed next to each other in opposite orientations) from the Barnes Complex. In this case the material was collected to preserve the original orientation of the sample.
Sparse florets of hydromagnesite (identified by EDS and morphology) can be found at or partially embedded into the surfaces of calcite rhombs (Fig. S5), indicating that hydromagnesite is a trace and late-precipitating phase but can be contemporaneous with calcite growth. Other observed features include co-occurring smooth calcite rhomb faces together with rough micro-stepped saddles (Fig. S6) suggestive of the effects of bacterially exuded bio-polymers (e.g. Lian et al. 2006; Tourney and Ngwenya 2009), associations with apparent bacterial colonies (Fig. S7) and aragonite needles featuring stacked steps (Fig. S8) that are suggestive of surface nucleation control of growth.

From the above observations, we infer the following growth stages for floes forming at the surface of high pH pools:

1. Nucleation of aragonite crystals, with horizontal sprays of aragonite crystals suspended by surface tension and forming the base for layer formation.
2. Bundles of aragonite crystals grow parallel to the water surface and downward into the water, forming hemispheres of crystals that merge to form a nearly continuous layer.
3. After aragonite, blocky rhombohedral calcite crystals form, nestled among aragonite hemispheres. Calcite can be seen overgrowing aragonite needles.
4. Late, but accompanying calcite growth, precipitation of hydromagnesite, Mg5(CO3)4(OH2)(H2O)5 or Dypingite, Mg5(CO3)4(OH2)(H2O)5. Eventually the floe sinks to the bottom of the pool when a mechanical disturbance breaks the surface tension (see suppl. mat. for the limit of surface tension on floe thickness). After sinking to the bottom of the pool, calcite growth can continue on the surface of broken floe fragments.

### 4.2. Chemistry of water samples

Elemental concentrations of water samples along with pH are presented in Table 2. The direct samples of springs and of pools have pH in the range of 11.3–12, and are characterized by relatively high Ca concentrations (12–58 ppm), high K concentrations (0.5–7 ppm), and low Mg concentrations (0.07–0.35 ppm). In contrast, samples of Austin Creek have pH in the range of 7.8–9.5 and are characterized by relatively low Ca concentrations (1.2–8 ppm), low K concentrations (0.06–0.7 ppm) and high Mg concentrations (41–49 ppm). The pool and spring water samples with pH ≥ 11.3 mostly have very low Mg/Ca molar ratios, less than 0.01, except for two samples of the Wedding Cake pool that have Mg/Ca ratios of 0.34 and 4.5. The creek samples have high Mg/Ca ranging from 8.5 to 66, which varies with pH, suggestive of mixing between creek water and spring water. Mixing models between creek water and spring water fit well the water samples with pH < 11 (Fig. 6), indicating that the chemical influence of spring water can be discerned in downstream creek samples.

### 4.3. δ44Ca of water samples

The high pH water samples range in δ44Ca from 0.02‰ up to 1.23‰. The low end of the range is similar to the δ44Ca of upper mantle peridotite (Huang et al., 2010) consistent with the Ca in the springs being derived from the serpentinization of the ultramafic rocks. The sample with the highest Ca concentration (58 ppm, Wedding Cake Seep) also has the lowest δ44Ca (0.02 ± 0.06‰), while the sample with the lowest Ca concentration (12 ppm, Wedding Cake Pool) has the highest δ44Ca (1.23 ± 0.06‰). This pattern in concentration and δ44Ca suggests an effect due to precipitation of calcium carbonate at the various sampling localities and times. To examine this, the isotopic data for the waters with pH > 11 (F1-F4, F7-F15) are used for Rayleigh distillation calculations (Fig. 7A). The slope of the best-fit line to the data (r2 = 0.91, p < 0.01) gives a calcium fractionation factor (Δ44Ca - δ44Ca of water) of −0.76 ± 0.12‰ (2σ), indicating that this is the average Ca isotope fractionation accompanying the removal of Ca2+ to calcium carbonate from the various waters at The Cedars. Below we compare this value to results for Δ44Ca derived from direct water/CaCO3 differences.

### 4.4. δ44Ca of calcium carbonate samples

The Ca isotope ratios (δ44Ca) of the calcium carbonates range from −0.77‰ to −0.17‰ (Table 3), with no correlation with either δ34S or δ18O (Fig. S9). The analyzed carbonates cover a range of textures and mineralogy. Because of their immediate association with water, the floe samples provide the best opportunities to directly measure fractionation (Δ44Ca) between calcium carbonate and dissolved Ca2+ arising from crystallization. We analyzed five water-floe pairs (Table 4), three from different pools at the BSC, and one each from the Wedding Cake and from the GPS. The average of all five pairs gives a Δ44Ca of...
4.5. $\delta^{18}O$ and $\delta^{13}C$ of calcium carbonate samples

Calcium carbonate $\delta^{18}O$ and $\delta^{13}C$ data are presented in Table 3 and Tables S1–S3, and displayed in Fig. 8 along with data for calcium carbonates from The Cedars analyzed by Meister et al. (2011). The $\delta^{18}O$ and $\delta^{13}C$ values of the carbonates of all textures fall along a roughly 1:1 line, far from the expected composition for calcium carbonate in Table 2.

![Table 2](image)

Ca isotopic and chemical compositions of waters from The Cedars.

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<th>Label</th>
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<th>$\pm 2\sigma$</th>
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<th>K, ppm</th>
<th>Mg, ppm</th>
<th>Na, ppm</th>
<th>Sr, ppm</th>
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<td>6.98</td>
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<td>57</td>
<td>3.3</td>
<td>0.0057</td>
<td>11.6</td>
</tr>
<tr>
<td>F13</td>
<td>BSC2 10/16</td>
<td>0.16</td>
<td>0.12</td>
<td>54.0</td>
<td>1.26</td>
<td>0.098</td>
<td>56</td>
<td>3.5</td>
<td>0.0030</td>
<td>11.7</td>
</tr>
<tr>
<td>F14</td>
<td>Pool E</td>
<td>0.27</td>
<td>0.21</td>
<td>41.7</td>
<td>1.57</td>
<td>0.198</td>
<td>57</td>
<td>3.1</td>
<td>0.0078</td>
<td>11.6</td>
</tr>
<tr>
<td>F15</td>
<td>Wedding Cake 9/16</td>
<td>0.14</td>
<td>0.11</td>
<td>47.8</td>
<td>0.76</td>
<td>9.8</td>
<td>20</td>
<td>3.5</td>
<td>0.338</td>
<td>11.3</td>
</tr>
<tr>
<td>4/14</td>
<td>Creek above Barnes Cpx</td>
<td>1.2†</td>
<td>0.06</td>
<td>49.0</td>
<td>1.37</td>
<td>66.0</td>
<td>7.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8/16</td>
<td>Creek above Barnes Cpx</td>
<td>3.1†</td>
<td>0.10</td>
<td>40.9</td>
<td>1.83</td>
<td>21.8</td>
<td>8.7</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>8/13</td>
<td>Creek below Camp</td>
<td>8.0†</td>
<td>0.67</td>
<td>41.1</td>
<td>2.17</td>
<td>8.52</td>
<td>9.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Ca concentrations by isotope dilution except those marked † that were conducted by Q-ICPMS. Other element concentrations by Q-ICPMS, pH measured in the field.

Fig. 6. Mixing model between creek and spring waters showing pH vs. Mg/Ca molar ratio. Curves model mixing between BSC Spring water (pH = 11.8, Mg/Ca = 0.002) and Austin Creek water (April at high-flow, upper grey curve, pH = 8.7, Mg/Ca = 66; August near low-flow, lower black curve, pH = 8.7; Mg/Ca = 22). The dashed horizontal line indicates a Mg/Ca ratio of 2.

$\Delta^{44}$Ca = $-0.76 \pm 0.12$‰, in good agreement with the value from the Rayleigh distillation calculation (Fig. 7B).

Fig. 7. (A) $\delta^{44}$Ca Rayleigh fractionation model plot for high-pH waters (>11.0) from The Cedars springs and pools. The value of F (the fraction of Ca remaining) is based on the water sample with the highest Ca concentration (58 ppm) and lowest $\delta^{44}$Ca (0.02 ± 0.06) from the seep above the Wedding Cake Pool (sample F9). The slope of the best-fit line gives a calcium isotope fractionation factor ($D^{44}$Ca) of $-0.76 \pm 0.12$‰ (2σ). (B) Summary of $\Delta^{44}$Ca determined from CaCO$_3$-water pairs (red circles) and the Rayleigh model shown in A for waters with pH $\geq$ 11.0.
Table 3
Ca, C, and O isotopic compositions of calcium carbonates.

<table>
<thead>
<tr>
<th>Label</th>
<th>Description</th>
<th>δ⁴⁴Ca_{BSC}, ‰</th>
<th>±2σ</th>
<th>δ¹³C_{VPDB}, ‰</th>
<th>δ¹⁸O_{VPDB}, ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carb A</td>
<td>Wedding Cake rim (4/5/14)</td>
<td>−0.46</td>
<td>0.09</td>
<td>−14.62</td>
<td>−4.24</td>
</tr>
<tr>
<td>Carb B</td>
<td>New Pool xtl strings #1 (10/11/14)</td>
<td>−0.17</td>
<td>0.10</td>
<td>−11.78</td>
<td>−3.76</td>
</tr>
<tr>
<td>Carb C</td>
<td>New Pool encrustation (10/11/14)</td>
<td>−0.46</td>
<td>0.11</td>
<td>−12.00</td>
<td>−3.65</td>
</tr>
<tr>
<td>Carb D</td>
<td>BSC floe, upstream (10/11/14)</td>
<td>−0.77</td>
<td>0.16</td>
<td>−26.19</td>
<td>−19.06</td>
</tr>
<tr>
<td>Carb E</td>
<td>BSC floe, middle (10/11/14)</td>
<td>−0.69</td>
<td>0.08</td>
<td>−26.73</td>
<td>−18.32</td>
</tr>
<tr>
<td>Carb F</td>
<td>BSC floe, downstream (10/11/14)</td>
<td>−0.52</td>
<td>0.19</td>
<td>−26.66</td>
<td>−18.79</td>
</tr>
<tr>
<td>Carb G</td>
<td>New Pool xtl strings #2 (10/11/14)</td>
<td>−0.42</td>
<td>0.11</td>
<td>−12.34</td>
<td>−4.80</td>
</tr>
<tr>
<td>Carb H</td>
<td>GPS floe (10/11/14)</td>
<td>−0.38</td>
<td>0.02</td>
<td>−21.39</td>
<td>−13.47</td>
</tr>
<tr>
<td>Carb I</td>
<td>BSC large floe sample (10/11/14)</td>
<td>−0.66</td>
<td>0.06</td>
<td>−26.71</td>
<td>−18.71</td>
</tr>
<tr>
<td>Carb J</td>
<td>GPS upper filtered carb (10/11/14)</td>
<td>−0.68</td>
<td>0.04</td>
<td>−13.48</td>
<td>−0.36</td>
</tr>
<tr>
<td>Carb K</td>
<td>GPS filtered carb (10/11/14)</td>
<td>−0.65</td>
<td>0.07</td>
<td>−13.54</td>
<td>−5.13</td>
</tr>
<tr>
<td>Carb L</td>
<td>GPS floe (8/3/13)</td>
<td>−0.41</td>
<td>0.10</td>
<td>−23.04</td>
<td>−14.74</td>
</tr>
<tr>
<td>Carb M</td>
<td>Wedding Cake 1 cm below rim (10/11/14)</td>
<td>−</td>
<td>−</td>
<td>−14.29</td>
<td>−3.56</td>
</tr>
<tr>
<td>Carb N</td>
<td>Wedding Cake 15 cm below rim (10/11/14)</td>
<td>−</td>
<td>−</td>
<td>−15.08</td>
<td>−4.58</td>
</tr>
<tr>
<td>Carb P</td>
<td>Pool E floe (PE-C1) (10/7/16)</td>
<td>−0.48</td>
<td>0.07</td>
<td>−27.55</td>
<td>−19.58</td>
</tr>
<tr>
<td>Carb Q</td>
<td>Wedding Cake Floe (9/2/16)</td>
<td>−0.58</td>
<td>0.11</td>
<td>−17.45</td>
<td>−6.69</td>
</tr>
<tr>
<td>Carb R</td>
<td>BSC2 Floe (10/7/16)</td>
<td>−0.52</td>
<td>0.07</td>
<td>−25.50</td>
<td>−18.77</td>
</tr>
</tbody>
</table>

Table 4
Calculated values of Ca isotopic fractionation due to carbonate precipitation using data from Tables 2 and 3 for floe/water pairs.

<table>
<thead>
<tr>
<th>Observation</th>
<th>δ⁴⁴Ca_{BSC}, ‰, ±2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rayleigh model with all high pH waters</td>
<td>−0.76 ± 0.12</td>
</tr>
<tr>
<td>Wedding Cake (Carb Q − F15)</td>
<td>−0.72 ± 0.16</td>
</tr>
<tr>
<td>BSC1 (Avg. of Carbs D,E,F, &amp; I minus F4)</td>
<td>−0.84 ± 0.11</td>
</tr>
<tr>
<td>BSC2 (Carb R-F13)</td>
<td>−0.68 ± 0.14</td>
</tr>
<tr>
<td>BSC Pool E (Carb P-F14)</td>
<td>−0.75 ± 0.22</td>
</tr>
<tr>
<td>GPS1 (Carb L-F1)</td>
<td>−0.67 ± 0.19</td>
</tr>
<tr>
<td>Weighted Average CaCO₂-Water</td>
<td>−0.75 ± 0.07</td>
</tr>
<tr>
<td>Weighted Average all values</td>
<td>−0.75 ± 0.06</td>
</tr>
</tbody>
</table>

5. DISCUSSION
5.1. Floe growth rate

The sample of floe material collected after eight days of growth (Fig. 3) had a thickness of ~20 μm and provides a constraint on the growth rate of calcium carbonate precipitation represented by floe formation on pool surfaces. The rate of calcium carbonate growth per square meter is provided by Eq. (1):

\[ R(\text{mol/m}^2/\text{s}) = (d \cdot \rho)/(M \cdot t) \]  

(1)

where \(d\) is the floe thickness (meters), \(\rho\) is the floe density (g/m³) taking into account porosity and the proportions of calcite and aragonite, \(M\) is the molecular weight of CaCO₃ (100.086 g/mole), and \(t\) is the time interval of growth (seconds). Given a thickness of ~20 μm, a growth time of eight days, a porosity of 0 to 40% (Fig. 4), and a mineral composition of 80% calcite and 20% aragonite, Eq. (1) yields a growth rate range of 4.8 \times 10^{-7} \text{ mol/m}^2/\text{s} to 8.0 \times 10^{-7} \text{ mol/m}^2/\text{s}. From this range in growth rate, an estimate can be made of the aragonite saturation state (\(\Omega\)) through the equation \(R = k(\Omega − 1)^n\) where the rate constant \(k\) is given for aragonite precipitation by the empirical relation \(\ln(k) = 11.54 − 8690/T\) (\(T\) in Kelvin) and the reaction order, \(n\), is 1.7 (Romanek et al. 2011). Applying this equation to the growth rate range at \(T = 17.4°C\) yields a \(\Omega\) of ~9–13. This compares well with the \(\Omega\) estimates made by Morrill et al. (2013) of ~13 for BSC (where our growth rate was measured) and ~5 for GPS based on measured ion chemistry.

The calculated range in aragonite growth rate, along with the average \(δ^{44/40}\text{Ca}\) value of −0.75 ± 0.07‰ derived above is plotted in Fig. 9 for comparison to synthetic calcite (Tang et al., 2008; Watkins et al., 2017), calcite travertine (Yan et al., 2016), and theoretical values based on the DePaolo (2011) surface reaction kinetic model for calcite. The result for The Cedars falls along the upper bound of the array of experimental data, suggesting that the growth rate-dependence is fairly consistent across a broad range of pH values.

The inferred growth rate for floe carbonate has implications for the rate of spring resupply to pools, in particular the main BSC pool. For a Ca concentration of 51.7 ppm in the spring water supply of the pool, the growth of each square centimeter of floe to a thickness of 25 μm would require between 43 and 53 ml (depending on density/porosity of the floe) of BSC spring water. The pool water
beneath floes represented by samples D, E, F and I had a calcium concentration of 51.1 ppm that is indistinguishable from the BSC spring sample taken at that time (51.7 ppm). Given the area of the pool (roughly 1.6 m²), a supply rate of fresh spring water to the pool of \( \frac{1}{C_{24}} \text{ml/s} \) (or \( \frac{1}{C_{24}} \text{85 L/day} \)) would be required in order to maintain both the Ca concentration and Ca isotope composition. At the Wedding Cake pool, the supply of fresh spring water can be limited relative to carbonate precipitation, since at times the Ca concentration can be driven down by a factor of \( \frac{1}{C_{24}} \text{5} \) relative to the spring source, and the Ca isotope composition of the pool can be fractionated (fluid F3 \( \delta^{44}\text{Ca} = 1.23 \text{‰} \)) by calcium carbonate precipitation.

The calcium carbonate growth rate inferred above is comparable to the expected flux of CO₂ from the atmosphere to the pool water. In a set of BaCO₃ precipitation experiments at pH = 10 using a hydroxide buffer, Usdowski and Hoefs (1986) measured a CO₂ flux of \( 4.7 \times 10^{-7} \text{ mol/m}^2/\text{s} \), which compared well to their own calculated estimate based on CO₂ diffusivity in water and the CO₂(aq) hydroxylation rate constant. The similarity between this value at pH 10 and our growth rate estimates for samples precipitated at pH > 10 suggests that calcium carbonate floe growth and uptake of atmospheric CO₂ are strongly coupled (see Section 5.3).

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Fig. 8. The carbon and oxygen isotopic compositions of carbonate samples from The Cedars. Open circles show data from Meister et al. (2011). Vertical arrows along the x-axis show the \( \delta^{13}\text{C} \) of total inorganic carbon (TIC) from a pool sample at the BSC, and TIC for a sample of Austin Creek (Morrill et al., 2013). Shown for reference is the isotopic composition of atmospheric CO₂ (Pt Arena, CA data from White et al., 2015) and an estimate for pre-industrial atmospheric CO₂. The black line shows the slope of a 1 to 1 correlation between \( \delta^{18}\text{O} \) and \( \delta^{13}\text{C} \), which is parallel to the blue dashed line provided for visual reference.

Fig. 9. Comparison of \( \Delta^{44}\text{Ca} \) vs crystal growth rate data between aragonite/calcite floes at The Cedars (this study), synthetic calcite (Tang et al., 2008; Watkins et al., 2017), modern calcitic travertine (Yan et al., 2016) and the DePaolo (2011) surface kinetic model for calcite. Error bars represent ±2σ intervals of the reported values.
5.2. Aragonite precipitation

We observed aragonite in all of our samples examined with XRPD or SEM, as did Meister et al. (2011) and O’Neil and Barnes (1971), including in pool rims, pool snow, pool floes and precipitates from mixed spring/creek waters (Table 1, Figs. 4 and 5, Figs. S1–S4). Meister et al. (2011) propose that aragonite at The Cedars is associated with high Mg/Ca molar ratios of the water resulting from mixing of high Mg/Ca ratio creek water with the low Mg/Ca spring water leading to a high enough Mg/Ca ratio to inhibit the precipitation of calcite in favor of metastable aragonite. Several direct observations argue against high Mg/Ca as the explanation for all occurrences of aragonite at The Cedars. The pools at the BSC produce floes of aragonite/calcite from solutions with very low Mg/Ca ratios (<0.01, see above and Table 2), with aragonite as the first phase to precipitate followed by calcite (Fig. 4). Likewise, the rims and snow of low Mg/Ca spring pools also contain aragonite. The high pH of spring pools is sensitive to additions of creek water with a pH of 7.8–8.7. Mixing models demonstrate that even with the addition of creek water with Mg/Ca = 21.8, the Mg/Ca of the mixture does not rise above 2 until the pH falls well below 11 (Fig. 6). Such pH values are not seen in the spring pools (pH range 11.3–12.0, Table 2). However, there are instances of aragonite occurring at locations where spring water enters the creek directly (e.g. Carb B and Carb C, see Suppl. Fig S2 and S3) where high Mg/Ca may play a role in favoring aragonite over calcite. Such samples, precipitating from clearly mixed spring/creek water (Carbs B and C in Table 3; Carbs S, T, Y and AA in Table S1; Samples labeled “mixed Spr/Cr” in Fig. 7), have C and O isotope compositions distinct from aragonite/calcite samples precipitated from spring water.

Alternative chemical variables that potentially can promote aragonite precipitation over calcite from cool springs include high pH and the degree of oversaturation (see review by Jones, 2017). Experiments by Tai and Chen (1998) demonstrate that the favored calcium carbonate polymorph is a function of solution pH. They found that at 24 °C that with pH below 10–10.5, vaterite is the favored polymorph to crystallize, while at pH ≥ 12–11.8 calcite is dominant, and for pH in the range of 10.5–11.5 aragonite was the dominant polymorph peaking in abundance at pH ~ 11.3. Similar effects of pH on carbonate polymorphism were found by Matsumoto et al. (2010). The degree of supersaturation has been shown by Kawano et al. (2009) to control polymorphism, with high (Ω > 15 at 20 °C) saturation favoring vaterite and at Ω < 15 favoring calcite. However, these experiments were likely conducted at circum-neutral pH (the pH conditions were measured but not given by Kawano et al., 2009) and so may be consistent with the experiments of Tai and Chen (1998) in which at a Ω of ~40 and pH < 10 vaterite precipitation was favored.

From the SEM observations of floes discussed above, the first phase to precipitate is aragonite, followed by calcite. This is consistent with the surface layer of the water having a pH of 11.0–11.5 and a Ω of 9–13 favoring the nucleation of aragonite over calcite. As the layer thickens it encounters a pH > 11.5 and calcite begins to nucleate and grow. In considering the preferred nucleation of aragonite in modern seawater, Sun et al. (2015) conclude based on ab initio calculations that aragonite is favored over calcite for Mg/Ca ratios in the solution greater than ~2 due to Mg incorporation stabilizing aragonite relative to calcite. We speculate that the effect of pH is to change the surface energy of calcium carbonate nuclei such that the aragonite nucleation rate is maximized at pH 11.0–11.5, whereas calcite nucleation and growth is promoted at higher pH.

5.3. Modeling of kinetic oxygen and carbon isotope fractionation

A significant advance of the past decade has been the development of quantitative models of kinetic isotope effects between precipitating calcium carbonate crystals and dissolved ions (DePaolo, 2011; Nielsen et al., 2012, 2013; Watkins et al., 2013, 2014, 2017; Devriendt et al., 2017) and between DIC species and water (Devriendt et al., 2017; Chen et al., 2018). Chen et al (2018) developed a model for oxygen and carbon isopes that integrates reaction kinetics of the DIC species, carbonate precipitation and fluid mixing - a combination that is necessary to understand alkaline springs like those at The Cedars. This model is informed by extensive experimental and theoretical work on the kinetics and isotope fractionations among DIC species (e.g. Usdowski et al., 1991; Clark et al., 1992; Usdowski and Hoefs, 1993; Zeebe and Wolf-Gladrow, 2001; Beck et al., 2005; Kim et al., 2006; Zeebe, 2014; Sade and Halevy, 2017, 2018) and carbonate minerals (Romanek et al., 1992; Kim et al., 2007; Wollters et al., 2012; Watkins et al., 2013, 2014). In this section, we present a model adapted from that of Chen et al (2018), with addition of diffusive effects at the atmosphere-water interface and use it to evaluate the observed C and O isotope variations, while also using the constraints we have on carbonate growth rates and Ca isotope compositions.

We begin with a conceptual model (Fig. 10) of the precipitation of surface floes for which we have observational constraints. The floe initiates growth with various nucleation events at the water–air interface as CO2 is absorbed from the atmosphere and dissolved into the water (O’Neil and Barnes, 1971; Meister et al. 2011), where it undergoes hydroxylation to form HCO3 with subsequent rapid and near-quantitative conversion to CO32. The precipitation of calcium carbonate to build the floes consumes much of the DIC coming from the atmosphere. The isotopic composition of the DIC (essentially all in the form of CO32-) is set by hydroxylation of the incoming atmospheric CO2 to extremely low δ13C and δ18O values, and remains at such values unless shifted by the addition of DIC from spring or creek water.

As the floe thickens, it eventually detaches and sinks, carrying with it some of the surface water (with DIC having low δ13C and δ18O) into the deeper pool. Hence, the deeper pool water from which the “snow” and rim carbonates precipitate contains some of its DIC from the boundary layer near the surface either by diffusion or by the fluid boundary layer physically detaching, sinking, and mixing with the deep water. Isotopic equilibration of the detached layer is
Fig. 10. Conceptual model for the evolution of calcium carbonate floes at the surface of high pH waters. Within the water surface layer (not shown to scale) aragonite nucleation/growth rates are greater than those of calcite, consistent with ~pH = 11 (Tai and Chen 1998). As the aragonite layer thickens down into the water below with pH ≥ 11.5 calcite nucleation/growth rates become greater than aragonite (Tai and Chen 1998) resulting in overgrowth by calcite rhombs. Through disturbance of the pool’s surface due to wind, falling debris, rain, etc. the surface tension is broken and the floe sinks to the bottom where continued calcite precipitation can occur. With the surface cleared, the process of floe formation begins again.

hindered by the high pH of the pool water, so the kinetic signature of the surface processes can be preserved for a long period of time—days to tens of days at pH = 11.5 (Usdowski et al., 1991).

This conceptual framework is used to construct a two-stage model for what is happening at The Cedars (Fig. 11). The first stage, hereafter referred to as the thin-film model, focuses on the diffusional boundary layer (~100 µm) at the pool-atmosphere interface. We solve a system of reaction–diffusion equations to compute the concentrations and isotopic compositions of DIC species present in the one-dimensional model domain. The results place constraints on the hydroxylation kinetic fractionation factors (KFF = (a-1)-1000), which are used for defining the isotopic composition of the equilibrated inorganic carbon (EIC = HCO₃⁻ + CO₃²⁻; Chen et al., 2018) flux in the second stage. The second stage, hereafter referred to as the box model, describes the isotopic composition of a well-mixed reservoir as a function of the following fluxes with distinct isotopic compositions: (1) an EIC flux from the detached surface layer, (2) a spring replenishment flux, (3) a low-pH (8.7) creek flux, and (4) a CaCO₃ precipitation flux. The box model also includes reactions among DIC species. The results are used to determine the environmental conditions required to produce the full δ¹⁸O-δ¹³C data array.

5.3.1. Thin-film model

For the thin-film model, we start with a pool having a pH of 11.5 and a low DIC concentration of ~0.035 mM, based on the value for a BSC water sample given by Morrill et al. (2013). With these specified pH and DIC values, all other carbonate parameters are calculated based on expressions given by Zeebe and Wolf-Gladrow (2001) and pK values from Millero et al. (2007). The pool is assumed to be isotopically equilibrated initially (Table 5) and at saturation with respect to calcite (Ω = 1), from which we calculate an initial Ca²⁺ concentration of 1.3 mM, in the range of 0.94 to 1.3 mM reported by Morrill et al. (2013).

The rate of CO₂ uptake from the atmosphere is determined by the contrast between the partial pressure (or fugacity) of the atmospheric CO₂ and the concentration of CO₂(aq) in the surface water of the pool. The exchange across the surface between the gas phase CO₂ and the water is assumed to be very fast in comparison to the diffusive transport of the CO₂ into the pool away from the surface; i.e., local equilibrium:

\[ [\text{CO}_2]_{\text{interface}} = K_0 \cdot f_{\text{CO}_2}. \] (2)

where \( K_0 \) is Henry’s constant (mol/kg-soln/atm) and \( f_{\text{CO}_2} \) is the fugacity of CO₂ (atm). For a 400 ppm atmosphere, this leads to \( [\text{CO}_2]_{\text{aq}} = 1.6 \times 10^{-3} \) moles/kg-soln which is several orders of magnitude higher than the concentration in the bulk pool. The incoming CO₂ is converted to HCO₃⁻ according to the following reactions (Chen et al. 2018):

\[
\begin{align*}
\text{CO}_2 + 2\text{H}_2\text{O} & \rightleftharpoons \text{HCO}_3^- + \text{H}^+ + \text{H}_2\text{O} \quad (\text{Reaction 1}) \\
\text{CO}_2 + \text{OH}^- & \rightleftharpoons \text{HCO}_3^- + \text{H}_2\text{O} \quad (\text{Reaction 2}) \\
^{13}\text{CO}_2 + 2\text{H}_2\text{O} & \rightleftharpoons \text{H}^{13}\text{CO}_3^- + \text{H}^+ + \text{H}_2\text{O} \quad (\text{Reaction 3}) \\
^{15}\text{CO}_2 + \text{OH}^- & \rightleftharpoons \text{H}^{15}\text{CO}_3^- \quad (\text{Reaction 4}) \\
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{H}^{18}\text{CO}_3^- + \text{H}^+ \quad (\text{Reaction 5}) \\
\text{CO}_2 + ^{18}\text{OH}^- & \rightleftharpoons \text{H}^{18}\text{CO}_3^- \quad (\text{Reaction 6}) \\
^{18}\text{CO}_2 + ^{18}\text{OH}^- & \rightleftharpoons \text{H}^{18}\text{CO}_3^- \quad (\text{Reaction 7}) \\
^{18}\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{H}^{18}\text{CO}_3^- + \text{H}^+ \quad (\text{Reaction 8})
\end{align*}
\]
The ratios of forward to backward rate constants are equal to the equilibrium constant for each reaction, as given in Table 6.

At high pH (>11), CO₂ hydroxylation is much faster than CO₂ hydration because of the high OH⁻ concentration. We nevertheless retain the hydration reactions for completeness. The increase in CO₂ and HCO₃⁻ at the surface establishes large concentration gradients that drive diffusion of DIC species downward through the thin film. At the base of the thin film (z = 100 μm), we assume the pool is well-mixed and able to maintain fixed concentrations of dissolved species. For simplicity we assume that all dissolved species diffuse at the same rate and that there is no isotopic fractionation by diffusion (Zeebe, 2011).

Table 5
Compilation of equilibrium fractionation factors (EFFs; T in Kelvin unless otherwise noted).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Equation</th>
<th>α (17.4 °C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon isotopes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂(g) → HCO₃⁻</td>
<td>-9.483 T⁻¹ + 1.02389</td>
<td>0.9913</td>
<td>Mook (1986)</td>
</tr>
<tr>
<td>CO₂(aq) → HCO₃⁻</td>
<td>-9.866 T⁻¹ + 1.02412</td>
<td>0.9902</td>
<td>Mook (1986)</td>
</tr>
<tr>
<td>CO₂⁻ → HCO₃⁻</td>
<td>-0.867 T⁻¹ + 1.00252</td>
<td>0.9995</td>
<td>Mook (1986)</td>
</tr>
<tr>
<td>CO₂(g) → Calcite</td>
<td>exp((-1.2416 * 10⁻³ + 1.2416 * 10⁻³) / 1000) T⁻¹</td>
<td>0.9886</td>
<td>Bottinga (1968)</td>
</tr>
<tr>
<td>Oxygen isotopes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂(aq) → H₂O</td>
<td>exp(2520 T⁻² + 0.01212)</td>
<td>1.0429</td>
<td>Beck et al. (2005)</td>
</tr>
<tr>
<td>HCO₃⁻ → H₂O</td>
<td>exp(2590 T⁻² + 0.00189)</td>
<td>1.0331</td>
<td>Beck et al. (2005)</td>
</tr>
<tr>
<td>CO₂⁻ → H₂O</td>
<td>exp(2390 T⁻² - 0.00270)</td>
<td>1.0259</td>
<td>Beck et al. (2005)</td>
</tr>
<tr>
<td>Calcite → H₂O</td>
<td>exp(29.777 / 1000)</td>
<td>1.0318</td>
<td>Coplen (2007), Watkins et al. (2013)</td>
</tr>
<tr>
<td>OH⁻ → H₂O</td>
<td>(1 + [23.5 - 0.0728(T_C-25)] / 1000⁻¹)</td>
<td>0.9765</td>
<td>Zeebe (2020)</td>
</tr>
<tr>
<td>or</td>
<td>(1 + [19.1 - 0.0455(T_C-25)] / 1000⁻¹)</td>
<td>0.9809</td>
<td>Zeebe (2020)</td>
</tr>
</tbody>
</table>

HC³¹⁸O⁻. The ratios of forward to backward rate constants are equal to the equilibrium constant for each reaction, as given in Table 6.

Fig. 11. Schematic diagram showing how the two stages of the isotopic model fit together. The thin-film model focuses on processes within the 100 μm diffusional boundary layer at the pool-atmosphere interface and tracks spatial variations in DIC species’ concentrations and isotopic compositions. The box model focuses on the larger scale of the bulk pools and how the DIC species’ concentrations and isotopic compositions vary as a function of three fluxes: (1) DIC from the thin film, (2) DIC replenishment from the spring water inflow and outflow, and (3) CaCO₃ precipitation.
### Table 6

**Constants and parameters used in the model.**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{spr}$</td>
<td>Spring mass flux</td>
</tr>
<tr>
<td>$[\text{DIC}]_{spr}$</td>
<td>Spring [DIC]</td>
</tr>
<tr>
<td>$[\text{Ca}^{2+}]_{spr}$</td>
<td>Spring $[\text{Ca}^{2+}]$</td>
</tr>
<tr>
<td>$[\text{Alk}]_{spr}$</td>
<td>Spring total alkalinity</td>
</tr>
<tr>
<td>$[\text{CO}<em>2]</em>{spr}$</td>
<td>Spring $[\text{CO}<em>2]</em>{aq}$</td>
</tr>
<tr>
<td>$[\text{EIC}]_{spr}$</td>
<td>Spring $[\text{HCO}_3^-] + [\text{CO}_2^-]$</td>
</tr>
<tr>
<td>$F_{cr}$</td>
<td>Creek mass flux</td>
</tr>
<tr>
<td>$[\text{DIC}]_{cr}$</td>
<td>Creek [DIC]</td>
</tr>
<tr>
<td>$[\text{Ca}^{2+}]_{cr}$</td>
<td>Creek $[\text{Ca}^{2+}]$</td>
</tr>
<tr>
<td>$[\text{Alk}]_{cr}$</td>
<td>Creek total alkalinity</td>
</tr>
<tr>
<td>$[\text{CO}<em>2]</em>{cr}$</td>
<td>Creek $[\text{CO}<em>2]</em>{aq}$</td>
</tr>
<tr>
<td>$[\text{EIC}]_{cr}$</td>
<td>Creek $[\text{HCO}_3^-] + [\text{CO}_2^-]$</td>
</tr>
<tr>
<td>$J_{\text{atm}}$</td>
<td>EIC flux through thin water film</td>
</tr>
<tr>
<td>$S_{\text{Apool}}$</td>
<td>Surface area of pool</td>
</tr>
<tr>
<td>$J_{\text{CaCO}_3}$</td>
<td>Carbonate precipitation rate (moles/m$^2$/s)</td>
</tr>
</tbody>
</table>

**Part I: Fluxes and elemental concentrations**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Reference/Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{spr}$</td>
<td>0.001 kg-soln/s</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{DIC}]_{spr}$</td>
<td>0.035 mM</td>
<td>Morrill et al. (2013)</td>
</tr>
<tr>
<td>$[\text{Ca}^{2+}]_{spr}$</td>
<td>1.3 mM</td>
<td>Morrill et al. (2013)</td>
</tr>
<tr>
<td>$[\text{Alk}]_{spr}$</td>
<td>2.6 mM</td>
<td>Calc. from DIC &amp; pH</td>
</tr>
<tr>
<td>$[\text{CO}<em>2]</em>{spr}$</td>
<td>$1.0 \times 10^{-9}$ mM</td>
<td>Calc. from DIC &amp; pH</td>
</tr>
<tr>
<td>$[\text{EIC}]_{spr}$</td>
<td>0.035 mM</td>
<td>Calc. from DIC &amp; pH</td>
</tr>
<tr>
<td>$F_{cr}$</td>
<td>Variable (kg-soln/s)</td>
<td>Morrill et al. (2013)</td>
</tr>
<tr>
<td>$[\text{DIC}]_{cr}$</td>
<td>2.9 mM</td>
<td>Morrill et al. (2013)</td>
</tr>
<tr>
<td>$[\text{Ca}^{2+}]_{cr}$</td>
<td>0.13 mM</td>
<td>Morrill et al. (2013)</td>
</tr>
<tr>
<td>$[\text{Alk}]_{cr}$</td>
<td>3.0 mM</td>
<td>Calc. from DIC &amp; pH</td>
</tr>
<tr>
<td>$[\text{CO}<em>2]</em>{cr}$</td>
<td>0.041 mM</td>
<td>Calc. from DIC &amp; pH</td>
</tr>
<tr>
<td>$[\text{EIC}]_{cr}$</td>
<td>2.89 mM</td>
<td>Calc. from DIC &amp; pH</td>
</tr>
<tr>
<td>$J_{\text{atm}}$</td>
<td>$6 \times 10^{-7}$ moles/m$^2$/s</td>
<td>Usowski &amp; Hoefs (1986)</td>
</tr>
<tr>
<td>$S_{\text{Apool}}$</td>
<td>1 m$^2$</td>
<td>-</td>
</tr>
<tr>
<td>$J_{\text{CaCO}_3}$</td>
<td>$J_{\text{CaCO}<em>3} = k</em>{\text{calc}}(\Omega - 1)^{1.7}$</td>
<td>Romanek et al. (2011)</td>
</tr>
<tr>
<td></td>
<td>$\ln k_{\text{rate}} = 11.54 - (8690/T_K)$</td>
<td>Romanek et al. (2011)</td>
</tr>
</tbody>
</table>

**Part II: Reaction rate constants**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>Fraction of HCO$_3^-$ in EIC</td>
</tr>
<tr>
<td>$k_{1s}$</td>
<td>Rate const. CO$_2$ hydration (s$^{-1}$)</td>
</tr>
<tr>
<td>$k_{1d}$</td>
<td>Rate const. CO$_2$ dehydration (M$^{-1}$s$^{-1}$)</td>
</tr>
<tr>
<td>$k_{1a}$</td>
<td>Rate const. CO$_2$ hydroxylation (M$^{-1}$s$^{-1}$)</td>
</tr>
<tr>
<td>$k_{1s}$</td>
<td>Rate const. CO$_2$ dehydroxylation (s$^{-1}$)</td>
</tr>
</tbody>
</table>

**Part III: Isotopic parameters**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Reference/Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{18}O_{\text{H}_{2}O}$</td>
<td>0.00199377</td>
<td>-</td>
</tr>
<tr>
<td>$\delta^{18}O_{\text{CO}_2}$ or (aq)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\delta^{18}O_{\text{EIC}}$</td>
<td>$\delta^{18}O_{\text{H}_{2}O}$</td>
<td>Pinse et al. (1956)</td>
</tr>
<tr>
<td>$\delta^{18}O_{\text{EIC}}$ or (aq)</td>
<td>$\delta^{18}O_{\text{H}_{2}O}$</td>
<td>Pinse et al. (1956)</td>
</tr>
<tr>
<td>$R_{\text{COC}(aq)}$</td>
<td>$[\text{C}^{18}\text{O}] / [\text{CO}_2]$</td>
<td>$K_3$ from Millero et al. (2007)</td>
</tr>
<tr>
<td>$R_{\text{EIC}}$</td>
<td>$[\text{^{13}EIC}] / [\text{^{18}EIC}]$</td>
<td>-</td>
</tr>
<tr>
<td>$^{18}\chi$</td>
<td>Fraction of $\text{H}^{18}\text{CO}_3^-$ in $^{18}\text{EIC}$</td>
<td>-</td>
</tr>
<tr>
<td>$k_{1s}^{18}$</td>
<td>Rate const. for $^{18}\text{CO}_2$ hydration (s$^{-1}$)</td>
<td>-</td>
</tr>
<tr>
<td>$k_{1d}^{18}$</td>
<td>Rate const. for $^{18}\text{CO}_2$ dehydration (M$^{-1}$s$^{-1}$)</td>
<td>-</td>
</tr>
<tr>
<td>$k_{1a}^{18}$</td>
<td>Rate const. for $^{18}\text{CO}_2$ hydroxylation (M$^{-1}$s$^{-1}$)</td>
<td>-</td>
</tr>
<tr>
<td>$k_{1s}^{18}$</td>
<td>Rate const. for $^{18}\text{CO}_2$ dehydroxylation (s$^{-1}$)</td>
<td>-</td>
</tr>
</tbody>
</table>

**Equilibrium constraint**

| $K_w$ from DOE (1994) | $^{18}O_{\text{SMOW}} = -5.7\%$ | Isotope ratio |
| - | Isotope ratio | Isotopologue ratio |
| - | Isotopologue ratio | Isotopologue ratio |

**Equilibrium constraint**

| Zeebe and Wolf-Gladrow (2001) | 0.087 | This study |
| - | 0.9829 | Equilibrium constraint |
| - | 0.9829 | Equilibrium constraint |
The combined process of reaction and diffusion is modeled by solving the following system of partial differential equations:

\[
\frac{\partial [\text{CO}_2]}{\partial t} = D_{\text{CO}_2} \left( \frac{\partial^2 [\text{CO}_2]}{\partial z^2} + \{ -k_{i,1}[\text{CO}_2] + k_{i,1}[\text{EIC}] \cdot \chi \cdot [\text{H}^+] \right) - k_{i,4}[\text{CO}_2][\text{OH}^-] + k_{i,4}[\text{EIC}] \cdot \chi \right) \quad (3)
\]

\[
\frac{\partial [\text{EIC}]}{\partial t} = D_{\text{EIC}} \left( \frac{\partial^2 [\text{EIC}]}{\partial z^2} + \{ k_{i,1}[\text{CO}_2] - k_{i,1}[\text{EIC}] \cdot \chi \cdot [\text{H}^+] \right) + k_{i,4}[\text{CO}_2][\text{OH}^-] - k_{i,4}[\text{EIC}] \cdot \chi \right) - Sp \cdot J_{\text{CaCO}_3} \quad (4)
\]

\[
\frac{\partial [\text{Ca}^{2+}]}{\partial t} = D_{\text{Ca}^{2+}} \left( \frac{\partial^2 [\text{Ca}^{2+}]}{\partial z^2} - Sp \cdot J_{\text{CaCO}_3} \right) \quad (5)
\]

\[
\frac{\partial [\text{Alk}]}{\partial t} = D_{\text{Alk}} \left( \frac{\partial^2 [\text{Alk}]}{\partial z^2} - 2 \cdot Sp \cdot J_{\text{CaCO}_3} \right) \quad (6)
\]

\[
\frac{\partial [^{13}\text{CO}_2]}{\partial t} = D_{^{13}\text{CO}_2} \left( \frac{\partial^2 [^{13}\text{CO}_2]}{\partial z^2} + \{ -k_{i,1}[^{13}\text{CO}_2] ight) + k_{i,4}[^{13}\text{CO}_2][\text{OH}^-] + k_{i,4}[^{13}\text{EIC}] \cdot \chi \right) \quad (7)
\]

\[
\frac{\partial [\text{C}^{18}\text{OO}]}{\partial t} = D_{\text{C}^{18}\text{OO}} \left( \frac{\partial^2 [\text{C}^{18}\text{OO}]}{\partial z^2} + \{ -b_{i,1}[\text{C}^{18}\text{OO}] \right) + 2/3 b_{i,1}[\text{EIC}] \cdot \chi \cdot [\text{H}^+] - b_{i,4}[\text{C}^{18}\text{OO}][\text{OH}^-] \right) + 2/3 b_{i,4}[\text{EIC}] \cdot \chi \right) \quad (8)
\]

\[
\frac{\partial [^3\text{EIC}]}{\partial t} = D_{^3\text{EIC}} \left( \frac{\partial^2 [^3\text{EIC}]}{\partial z^2} + \{ +3/a_i[\text{CO}_2]r_w \right) - 1/3 a_i[^3\text{EIC}] \cdot \chi \cdot [\text{H}^+] \right) + a_i[\text{CO}_2][\text{OH}^-] - 1/3 a_i[^3\text{EIC}] \cdot \chi \right) + b_{i,1}[\text{C}^{18}\text{OO}] - 2/3 b_{i,1}[\text{EIC}] \cdot \chi \right) \cdot [\text{H}^+] + b_{i,4}[\text{C}^{18}\text{OO}][\text{OH}^-] \right) - 2/3 b_{i,4}[\text{EIC}] \cdot \chi \right) - Sp \cdot J_{\text{CaCO}_3} \quad (9)
\]

\[
\frac{\partial [^3\text{EIC}]}{\partial t} = D_{^3\text{EIC}} \left( \frac{\partial^2 [^3\text{EIC}]}{\partial z^2} + \{ [-a_i[\text{CO}_2]r_w \right) - 1/3 a_i[^3\text{EIC}] \cdot \chi \cdot [\text{H}^+] \right) + a_i[\text{CO}_2][\text{OH}^-] - 1/3 a_i[^3\text{EIC}] \cdot \chi \right) + b_{i,1}[\text{C}^{18}\text{OO}] - 2/3 b_{i,1}[\text{EIC}] \cdot \chi \right) \cdot [\text{H}^+] + b_{i,4}[\text{C}^{18}\text{OO}][\text{OH}^-] \right) - 2/3 b_{i,4}[\text{EIC}] \cdot \chi \right) - Sp \cdot J_{\text{CaCO}_3} \quad (10)
\]

where \( D_i \approx 1\times10^{-9} \text{ m}^2/\text{s} \) is the diffusivity of species \( i \), \( \chi \) is the fraction of EIC that is HCO\(_3\), \( J_{\text{CaCO}_3} \) is the growth rate of CaCO\(_3\) (mol/m\(^2\)/s), Sp is the specific reactve surface area (m\(^2\)/kg-soln), and \( r_w \) is the \(^{18}\text{O}/^{16}\text{O} \) of water. Reaction terms are set apart by braces \( \{ \). Following Chen et al. (2018), we write CO\(_2\) and HCO\(_3\) together as EIC, assuming instantaneous isotopic equilibration between these two species because they equilibrate on a timescale of 10\(^{-7}\) sec (Zeebe and Wolf-Gladrow, 2001). The pH is calculated in the model at each time step from [DIC] and Alk, assuming instantaneous pH adjustment to these quantities. The time
required to establish steady state in the thin film is short, less than 30 seconds, owing to the small length scale of the domain (Fig. S11).

Steady state profiles are displayed in Fig. 12. The only parameter we treat as adjustable is the specific reactive surface area (Sp), which dictates the efficiency of CaCO₃ precipitation. A large Sp implies many crystal nuclei and/or rough crystal surfaces and leads to lower steady state Ω values because a large precipitation flux prevents DIC accumulation (Fig. 12f). In the absence of any constraints on Sp, we report that Sp ~ 200 ± 100 m²/kg-soln yields pH, growth rate, and Ω profiles that are most consistent with our estimates based on floe thickness and growth rate calculations (Fig. 12i), but note that a wide range of Sp values (10–1000) can be accommodated by the data.

The CO₂ flux from the atmosphere is governed by the concentration gradient of CO₂, which is very large near the surface since the CO₂ in the water is close to zero (Fig. 12a). The diffusive flux of CO₂ into the deeper pool is very small because CO₂ hydroxylates faster than it can diffuse. The increase in DIC and removal of Ca²⁺ to CaCO₃ both lower the pH near the surface (Fig. 12k). Although the pH is lower, the degree of calcite supersaturation is highest near the surface (Fig. 12f) because the increase in DIC more than offsets the DIC speciation effects caused by lower pH.

The model accounts for isotopic distillation of reactants as they are converted to products. This is clearly seen in the δ¹³C profile for CO₂ (Fig. 12g) where isotopically light CO₂ has been removed by hydroxylation, leaving behind a residual CO₂ pool with very low concentration that is extremely isotopically heavy. The abrupt return to the initial value at z = −100 is a consequence of the fixed concentration boundary condition in the model. Isotopic distillation does not occur for the δ¹⁸O of CO₂ (Fig. 12d) because the KFF is set at θ‰, as discussed further below.

5.3.2. CO₂ hydroxylation KFFs

The thin-film model is used to inform our estimates of the kinetic fractionation factors (KFFs) related to CO₂(aq) hydroxylation, which represents the instantaneous isotopic fractionation between the reactant CO₂(aq) (for carbon KFF) or ‘CO₂(aq) + OH⁻’ (for the bulk oxygen KFF) and the product HCO⁻₃. To begin, it is important to note that the CO₂ hydroxylation reaction is essentially unidirectional in the upper 60 μm of the model domain, where the ratio of forward to backward reaction rates is ~1000 (Fig. 12c). This implies that the full kinetic fractionation is expressed in the EIC prior to it being converted to CaCO₃. There is, however, an additional kinetic fractionation attending the CaCO₃ precipitation reaction that depends on the degree of supersaturation through an equilibration index Eₜ (Devriendt et al., 2017). Since the degree of supersaturation is relatively modest for Sp > 10 m²/kg, the precipitation reaction is bi-directional and the precipitating CaCO₃ is isotopically heavier than CO₂. This drives the isotopic composition of EIC to an isotopically lighter composition than that set by the kinetic limit of hydroxylation (Fig. 12c, h, and i).

The best-fit hydroxylation KFFs depend on the degree of distillation of EIC as it is converted to CaCO₃, which in turn depends on Sp (Fig. 12e and h). A small Sp leads to a small fraction of the CO₂ convert to CaCO₃. In this scenario, the dissolved CO₂ records the KFF and the CaCO₃ is offset to heavier values (Fig. 12i). By contrast, for Sp > 100, most of the CO₂ is converted to CaCO₃ and in this scenario, the CaCO₃ records the KFF while the CO₂ is offset to even lighter values (Fig. 12l). It may be significant that the one measurement of δ¹³C of BSC pool water DIC gives a value of −31.5‰ (VPDB; Morrill et al., 2013), which is about 5‰ lighter than the lightest values recorded by the CaCO₃ and consistent with near complete conversion of CO₂ to CaCO₃. This suggests that, instead of the EIC, it is the solid CaCO₃ that records the CO₂ hydroxylation KFF. If indeed there is a near quantitative transfer of the EIC to CaCO₃, the carbon and oxygen KFFs estimated from the δ¹⁸O and δ¹³C of floe samples should be unaffected by their varying proportions of calcite versus aragonite.

Using the δ¹³C values of floes at BSC and of local atmospheric CO₂ for the period 2013–2018 (NOAA CO₂ station Trinidad Head, USA- White et al., 2015), the carbon KFF related to CO₂ hydroxylation is estimated here to be −17.1 ± 0.8‰ relative to CO₂(aq) at 17.4 ± 1.0 °C. Following the same reasoning as for carbon isotopes, a bulk oxygen KFF is estimated at −0.4 ± 1.5‰ relative to CO₂(aq) + OH⁻. The oxygen KFF calculated relative to CO₂(aq) + OH⁻ relies on the accuracy of the OH⁻/H₂O oxygen EFF. A value of −21.3 ± 2.2‰ relative to H₂O for the equilibrium isotopic composition of OH⁻ was used based on quantum-chemical calculations (Zeebe, 2020). Since the isotopic composition of H₂O can be directly measured with high accuracy, and since the OH⁻/H₂O oxygen EFF is likely to be refined in the future, we also report the KFF relative to the sum of CO₂(aq) + H₂O (KFF* = −7.1 ± 1.1‰).

Kinetic isotope effects of similar magnitude have also been reported for a range of natural and synthetic carbonates formed in high pH solutions with gaseous CO₂ as the main DIC source. We reviewed the literature to compile a set of carbon and oxygen KFFs within a consistent framework. The revised KFF values listed in Table 7 and were calculated by taking into consideration the following:

(i) The temporal and geographical variability in the δ¹³C and δ¹⁸O of atmospheric CO₂ (Trolier et al., 1996; Keeling et al., 2001) for studies where the DIC source was atmospheric CO₂.

(ii) CO₂(g) distillation effects were corrected for in (semi-) closed system experiments (where possible) while an infinite CO₂ pool was assumed for fully open experiments.

(iii) Values for the equilibrium fractionation factors (EFFs) between CO₂(aq) and CO₂(g) of −1.1‰ and −0.3‰ were applied for carbon (Vogel et al., 1970) and oxygen (Beck et al., 2005; Barkan and Luz, 2012) isotopes, respectively.
For carbon isotopes, laboratory experiments suggest a KFF between $-11.8 \pm 0.5\%$ and $-17.0 \pm 0.5\%$ (Table 7, Fig. 13a; Craig, 1953; Usdowski and Hoefs, 1986; Clark et al., 1992; Dietzel et al., 2009; Böttcher et al., 2018) while field data suggest a very consistent KFF of between $-16.9\% \pm 1.3\%$ and $-17.2 \pm 0.6\%$ (Table 7, Fig. 13a; Clark et al., 1992; Mervine et al., 2014; Falk et al., 2016; this study). Only three studies suggest a significantly lower carbon
Table 7
Compilation of CO$_2$ hydroxylation KFF’s.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Study type</th>
<th>Mineral</th>
<th>T (°C)</th>
<th>pH</th>
<th>$\delta^{13}$C (% VPDB)</th>
<th>Carbon KFF*</th>
<th>$\delta^{18}$O (% VSMOW)</th>
<th>Oxygen bulk KFF*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
</tr>
<tr>
<td>Craig (1953)</td>
<td>Lab</td>
<td>Witherite</td>
<td>20</td>
<td>3</td>
<td>?</td>
<td>–13.7</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>USDowski &amp; Hoefs (1986)</td>
<td>Lab</td>
<td>Witherite</td>
<td>18</td>
<td>1</td>
<td>10.0</td>
<td>–7.7</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Clark et al. (1992)</td>
<td>Lab</td>
<td>Witherite</td>
<td>22</td>
<td>2</td>
<td>&gt;11.5</td>
<td>–13.9</td>
<td>1.1</td>
<td>–</td>
</tr>
<tr>
<td>Clark et al. (1992)</td>
<td>Lab</td>
<td>Witherite</td>
<td>22</td>
<td>2</td>
<td>12.8</td>
<td>–16.2</td>
<td>0.1</td>
<td>–</td>
</tr>
<tr>
<td>Dietzel et al. (2009)</td>
<td>Lab</td>
<td>Calcite</td>
<td>5</td>
<td>1</td>
<td>10.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Böttcher et al. (2018)</td>
<td>Lab</td>
<td>Witherite</td>
<td>4</td>
<td>1</td>
<td>12.4</td>
<td>–8.6</td>
<td>0.5</td>
<td>–</td>
</tr>
<tr>
<td>Böttcher et al. (2018)</td>
<td>Lab</td>
<td>Witherite</td>
<td>21</td>
<td>1</td>
<td>12.4</td>
<td>–8.6</td>
<td>0.5</td>
<td>–</td>
</tr>
<tr>
<td>Clark et al. (1992)</td>
<td>Field</td>
<td>Calcite</td>
<td>28</td>
<td>6</td>
<td>11.5</td>
<td>–7.5</td>
<td>1.1</td>
<td>–</td>
</tr>
<tr>
<td>Clark et al. (1992)</td>
<td>Field</td>
<td>Calcite</td>
<td>28</td>
<td>6</td>
<td>11.5</td>
<td>–7.5</td>
<td>1.1</td>
<td>–</td>
</tr>
<tr>
<td>Mervine et al. (2014)</td>
<td>Field</td>
<td>Calcite</td>
<td>28</td>
<td>6</td>
<td>11.0</td>
<td>–8.6</td>
<td>0.2</td>
<td>–</td>
</tr>
<tr>
<td>Falk et al. (2016)</td>
<td>Field</td>
<td>Arag. &amp; calcite</td>
<td>27</td>
<td>5</td>
<td>11.7</td>
<td>–8.6</td>
<td>0.2</td>
<td>–</td>
</tr>
<tr>
<td>This study</td>
<td>Field</td>
<td>Arag. &amp; calcite</td>
<td>17</td>
<td>1</td>
<td>11.0</td>
<td>–8.6</td>
<td>0.4</td>
<td>–</td>
</tr>
</tbody>
</table>

* Note: KFFs are expressed as $\varepsilon = (a-1) \times 1000$.  

a Keeling et al. (2001), station La Jolla (CA, USA).  
c average modern crust 'NJ' samples.  
d average modern crust 'clinic' samples.  
e average of two lowest 'crust' samples.  
f average of 'WHOI surface film' samples.  
g average 'WHOI surface film' samples.  
h average 'WHOI surface film' samples.  
i average of 'BSC flocs' samples.  
j average 'BSC flocs' samples.  
k CO$_2$(aq)–CO$_2$(g) carbon fractionation of 1.1‰ from Vogel et al. (1970).  
l corrected for distillation effect.  
m CO$_2$–H$_2$O isotopic equilibrium assumed.  
n calculated with OH$^-$–H$_2$O EFF values from Zeebe (2020).
KFF than −17‰ (Craig, 1953; the open system experiment of Clark et al., 1992; 4°C experiments of Böttcher et al., 2018). Lower apparent KFF in laboratory studies may be caused by a distillation of the CO₂ source or thermal differences between compressed air from the laboratory and the solution. Alternatively, the carbon KFF may be negatively correlated with temperature (Fig. 13a, r² = 0.53, p-value = 0.01), though this hypothesis is not supported by theoretical work (Guo, 2019). Based on field studies alone, where atmospheric CO₂ distillation is unlikely to occur, our best estimate for the carbon KFF related to the CO₂ hydroxylation reaction is −17.0 ± 0.3‰ (2σ; n = 5) over the 17–28°C temperature range.

For oxygen isotopes, most studies suggest a bulk KFF close to zero or slightly negative expressed relative to the sum of reactants ‘CO₂∕H₂O’ (KFF*, Fig. 13c) to avoid the uncertainty related to the calculated 18O∕16O ratio of OH⁻. The KFF* from field studies average −6.6 ± 0.9‰ over the 17–28°C temperature range. The lower KFF* calculated from the experimental result at 5°C (Böttcher et al., 2018) may indicate a positive temperature effect on the KFF* of ~0.14‰/°C but this result will need confirmation with additional data. Such a temperature dependence would be in part caused by the effect of temperature on the OH⁻∕H₂O oxygen EFF (i.e. ~+0.06%/°C; Zeebe, 2020).

5.3.3. Box model for the pools

The thin-film model is useful for quantifying the hydroxylation KFFs and understanding the isotopically light end of the array. To understand the overall trend we consider the different sources of DIC and forms of carbonate precipitating in the pools as a whole. Unlike the thin film at the surface, it takes much longer than 30 seconds to establish steady state in the larger volume (10–1000 L) pools. For this part of the system we apply a box model with four steady state in the larger volume (10–1000 L) pools. For

\[
\frac{\partial[CO_2]}{\partial t} = \text{(reaction terms, Eq. (3))} + \frac{F_{spr}}{V_{pool}}
\]

\[
\times ([CO_2]_{spr} - [CO_2]) + \frac{F_{ex}}{V_{pool}} ([CO_2]_{cr} - [CO_2])
\]

\[
\frac{\partial[EIC]}{\partial t} = \text{(reaction terms, Eq. (4))}
\]

\[
+ \frac{J_{atm} \cdot S_A}{V_{pool}} + \frac{F_{spr}}{V_{pool}} ([EIC]_{spr} - [EIC])
\]

\[
+ \frac{F_{ex}}{V_{pool}} ([EIC]_{cr} - [EIC]) - J_{CaCO_3} \cdot Sp
\]

\[
\frac{\partial[Ca^{2+}]}{\partial t} = \frac{F_{spr}}{V_{pool}} ([Ca^{2+}]_{spr} - [Ca^{2+}]) + \frac{F_{ex}}{V_{pool}}
\]

\[
\times ([Ca^{2+}]_{cr} - [Ca^{2+}]) - J_{CaCO_3} \cdot Sp
\]

\[
\frac{\partial[Alk]}{\partial t} = \frac{F_{spr}}{V_{pool}} ([Alk]_{spr} - [Alk]) + \frac{F_{ex}}{V_{pool}} ([Alk]_{cr} - [Alk]) - 2 \cdot J_{CaCO_3} \cdot Sp
\]

\[
\frac{\partial[^{13}CO_2]}{\partial t} = \text{(reaction terms, Eq.7)} + \frac{F_{spr}}{V_{pool}}
\]

\[
\times ([^{13}CO_2]_{spr} - [^{13}CO_2]) + \frac{F_{ex}}{V_{pool}}
\]

\[
\times ([^{13}CO_2]_{cr} - [^{13}CO_2])
\]

\[
\frac{\partial[^{18}OO]}{\partial t} = \text{(reaction terms, Eq. (9))} + \frac{F_{spr}}{V_{pool}}
\]

\[
\times ([^{18}OO]_{spr} - [^{18}OO]) + \frac{F_{ex}}{V_{pool}}
\]

\[
\times ([^{18}OO]_{cr} - [^{18}OO])
\]

\[
\frac{\partial[^{18}EIC]}{\partial t} = \text{(reaction terms, Eq. (10))}
\]

\[
+ \frac{J_{atm} \cdot S_A}{V_{pool}} \cdot ([^{18}EIC]_{hydrox}) + \frac{F_{spr}}{V_{pool}}
\]

\[
\times ([^{18}EIC]_{spr} - [^{18}EIC]) + \frac{F_{ex}}{V_{pool}}
\]

\[
\times ([^{18}EIC]_{cr} - [^{18}EIC]) - J_{CaCO_3} \cdot Sp \cdot \frac{[^{18}EIC]}{[EIC]} \cdot (^{13}CaCO_3-EIC)
\]

\[
\frac{\partial[^{13}CaCO_3]}{\partial t} = \frac{[^{13}CaCO_3]}{[EIC]} \cdot (^{13}CaCO_3-EIC)
\]
The atmospheric DIC flux is displayed in Fig. 14. In each panel there are three curves for different values of \( \Delta \) atm = 6 atm and \( \Delta \) pool = 100L. This value of \( \Delta \) is much smaller than the value used in the thin-film model because \( \Delta \) pool \( \gg \) \( \Delta \) film and there is a much higher surface area density of CaCO3 in the thin film than in the bulk pool. The atmospheric DIC flux is \( F_{\text{atm}} = 6 \times 10^{-7} \) mol/s, which is much greater than the spring DIC replenishment flux of \( F_{\text{spring}} \). The isotopic results are not sensitive to the \( \delta^{13}C \) of spring water because of its low DIC concentration. The spring flux still plays an important role, however, because it resupplies dissolved Ca\(^{2+}\) at a rate of 1.5 \times 10^{-6} \) mol/s, which is comparable to the DIC flux from the atmosphere.

The results of running the model to steady state for different values of \( F_{\text{spring}} \) at constant \( F_{\text{atm}} \) and \( F_{\text{spring}} \) are displayed in Fig. 14. In each panel there are three curves corresponding to different initial pH values of the pool (Fig. 14a). The change in steady state pH, Ca\(^{2+}\), and [DIC] occurs approximately where \( F_{\text{spring}} \) overtakes \( F_{\text{atm}} \) (Fig. 14a–c). The steady state \( \Omega \) and surface area normalized growth rate can be tuned by adjusting \( \Delta \) pool, \( \Delta \) film, and \( V_{\text{film}} \) (Supplement), but since these parameters have a limited effect on the overall isotopic results, they will not be discussed further.

The isotopic results of the box model are displayed in Fig. 14f and Fig. 15. The light endmember of the array corresponds to low \( F_{\text{spring}}/F_{\text{atm}} \). As the creek DIC flux increases, the pH decreases (shown by red circled numbers for the pH = 12.0 case in Fig. 15) and the \( \delta^{18}O/\delta^{13}C \) values move away from the kinetic limit and up the 1:1 line. Importantly, the pH remains above 11 for the entire part of the array below the equilibrium calcite line. The extreme heavy end of the array corresponds to high \( F_{\text{spring}}/F_{\text{atm}} \) and steady state pH values below ~11. An outcome of mixing of creek DIC to the high pH pool is that the oxygen isotopic composition of HCO3\(^-\) can become isotopically distilled to higher-than-equilibrium values as it is converted to the isotopically lighter CO2\(^2\). This can account for the cluster of carbonate samples exhibiting higher-than-equilibrium values. The extent of distillation is particularly sensitive to the initial pH, or more generally, the relative alkalinites of the spring versus creek water.

In Fig. 15, the CO2 distillation trajectory illustrates what would occur if all incoming atmospheric CO2 were to undergo hydroxylation without an opportunity for atmospheric equilibration exchange. The isotopic data show no evidence to support this, indicating that CO2 exchanges with the atmosphere faster than it is hydroxylated into HCO3\(^-\). This result supports the local equilibrium assumption in the thin-film model and our treatment in the box model of CO2 entering the bulk pool as EIC with an isotopic composition reflecting the kinetic limit of CO2 hydroxylation. The DIC equilibration trajectory shows the isotopic behavior of the EIC as the ratio between HCO3\(^-\) dehydroxylation and CO2 hydroxylation increases from 0 to 1. The isotopic data show no evidence of partial equilibration, indicating that the HCO3\(^-\) dehydroxylation rate is negligible relative to the CO2 hydroxylation rate. This is supported by modeling results, which indicate that an unrealistic \( V_{\text{pool}}/\Delta \) pool > 1000 is required in the model framework to yield an appreciable equilibration trajectory (Fig. S12).

5.4. Comparison to Oman carbonates

A quantitative understanding of the calcium carbonate \( \delta^{13}C/\delta^{18}O \) array at the Cedars enables us to explain the similarities and differences in isotopic data between carbonates from the Cedars (Fig. 8) and from Oman (Fig. 1). The \( \delta^{18}O/\delta^{13}C \) slopes from these two arrays are indistinguishable and follow a 1:1 line but there are noteworthy differences. The highest \( \delta^{18}O \) and \( \delta^{13}C \) values in the Oman array are about 5‰ and 8‰ greater than at The Cedars, respectively. The higher heavy end-member of Oman carbonates can be explained by higher and more variable atmospheric/surface water \( \delta^{18}O \) and DIC \( \delta^{13}C \) (large area of 50 x 200 km, Falk et al., 2016). In contrast, there are only minor differences in the light isotope limits between the Cedars (min \( \delta^{13}C \) ~ −27‰, min \( \delta^{18}O \) ~ −20‰) and Oman.
Fig. 14. Box model results for pools of high pH water at The Cedars. (a)-(f) Steady state composition of the pool as a function of $F^*_{\text{creek}}$ at fixed $F^*_{\text{spring}}$ and $F^*_{\text{atm}}$.

Fig. 15. Box model results for pools of high pH water at The Cedars using the same parameters as in Fig. 14. The circles with red numbers represent the pH values along the pH ini = 12 curve and show that pH remains high along the full array. Higher-than-equilibrium calcite forms when HCO$_3^-$ from the creek is isotopically distilled during conversion to CO$_3^{2-}$, which is then inherited by the CaCO$_3$. The green arrows show the trajectories of DIC equilibration and CO$_2$ distillation (all incoming CO$_2$ converted to HCO$_3^-$) for comparison.
spheric CO₂ had a heavier, pre-industrial composition is that these carbonates formed at a time when atmospheric CO₂ hydroxylation (Section 5.3.2). Modern carbonates forming in alkaline springs at the atmosphere-water interface therefore record the carbon isotopic composition of atmospheric CO₂. For the δ¹³C light end-member, differences between sites are also expected to be small since the δ¹³C of atmospheric CO₂ is also very similar in temperate and tropical regions (Trolier et al., 1996). However, calcium carbonates formed from hydroxylated CO₂ obtain one oxygen atom from OH⁻, making their δ¹⁸O value moderately sensitive to the solution δ¹³O. A ~ 5‰ difference in water δ¹³O between the Cedars and Oman springs (based on the heavy δ¹³O end-members) would result in a difference of ~ 1.7‰ for the light δ¹³O end-members, in good agreement with the observed ~ 2‰ difference between sites. Additional differences in the light end-members for oxygen isotopes may be caused by a temperature effect on the CO₂ hydroxylation KFF but this is not yet resolved.

5.5. Potential paleoenvironmental applications

The samples from old (unknown age) laminated calcium carbonate from BSC are shifted to the right of the array of modern carbonates (Fig. 8 and Fig. 15). A likely explanation is that these carbonates formed at a time when atmospheric CO₂ had a heavier, pre-industrial δ¹³C value, as depicted in Fig. 8. This feature of the data suggests that the δ¹³C of pre-industrial atmospheric CO₂ may be recoverable from ancient travertine, some of which is as old as 7000 years at The Cedars (¹⁴C ages 950–7100 years, Table S4).

The δ¹⁸O values of old travertines and most modern travertines are close to the end-member δ¹⁸O value reflecting HCO₃⁻ isotopically equilibrated with creek water (based EFF values from Beck et al., 2005). This suggests surface water DIC is the dominant carbon supply to travertine formation at The Cedars (rather than atmospheric CO₂). Hence, old travertines δ¹⁸O at The Cedars are expected to primarily reflect the oxygen isotope composition of past precipitation and surface/creek water temperature.

6. CONCLUSIONS

We investigated the textural and isotopic characteristics of carbonates that precipitate from ultrabasic (pH ~ 11–12) spring pools at The Cedars, California. The pools are fed by spring waters that have low [DIC] and relatively high Mg/Ca, and relatively high [Ca²⁺] as a consequence of serpentinization and Mg-carbonate precipitation in the subsurface. Once the spring water reaches the surface, CO₂ from the atmosphere enters and a thin film of CaCO₃ crystallizes and is held in place by surface tension. The initial polymorph to crystallize is aragonite, followed by calcite on the underside of the floe as it thickens. The preference of aragonite over calcite in this case is likely controlled by pH and not by high Mg/Ca ratio or high supersaturation.

Calcium isotopic fractionation between CaCO₃ and the host solution is sensitive to growth rate. The Δ⁴⁰/Ca values retrieved from five carbonate-water pairs are indistinguishable, with an average value of ~ 0.75 ± 0.07‰ (±95% confidence). The CaCO₃ growth rates are based on thickness measurements of surface floes of known age and are estimated to be the range of 4.8 × 10⁻³ mol/m²/sec to 8.0 × 10⁻³ mol/m²/sec. This value is in good agreement with the growth rate dependence of Δ⁴⁰/Ca determined from laboratory experiments (Tang et al., 2008; Watkins et al., 2017) and modeling (DePaolo, 2011; Nielsen et al., 2012).

Calcium carbonates display an extreme range (~20‰) in carbon and oxygen isotope compositions. The δ¹³C and δ¹⁸O values co-vary along a 1:1 line which trends toward the isotopic composition of isotopically equilibrated DIC from surface waters and pointing toward atmospheric CO₂. Most of the samples are lower in δ¹³C, some by as much as 15‰, than the expected equilibrium value at 17.4 °C. The extreme light isotope enrichments are an expression of the isotopically light OH⁻ ions combining with incoming CO₂ to form HCO₃⁻. The HCO₃⁻ rapidly deprotonates and is nearly quantitatively converted to CO₂⁺ ions, which then react with Ca²⁺ to precipitate CaCO₃. We estimate the hydroxylation KFF’s to be about ~17‰ relative to CO₂(aq) for carbon isotopes and ~7‰ relative to CO₂(aq) + H₂O⁻ for oxygen isotopes. These compare favorably to other estimates based on analysis of natural samples, but discrepancies remain between field and laboratory studies.

We adapted the kinetic isotopic fractionation model from Chen et al. (2018) to further investigate mechanisms of carbonate precipitation and kinetic isotope fractionation. The DIC in solution evolves chemically and isotopically according to the reaction rate equations in the CaCO₃-DIC-H₂O system. Using known (or reasonably well constrained) isotope-specific reaction rate constants, along with values for the fluxes that are constrained from the literature and our own measurements, the model reproduces the 1:1 co-variation if (1) the residence time of DIC in solution is much shorter than the equilibrium time; (2) CO₂ exchange with the atmosphere is efficient so that the incoming CO₂ does not become isotopically distillated when being converted to HCO₃⁻; and (3) the isotopic composition of the isotopically equilibrated spring and creek waters also lies near the 1:1 line defined by the composition of atmospheric CO₂ and the isotopically lightest data points. The model can also match the observation that some of the carbonates are isotopically heavier than the equilibrium value, owing to isotopic distillation of HCO₃⁻ from creek water as it is nearly quantitatively converted to CO₂⁺ during mixing with pool water.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data and information to this article can be found online at https://doi.org/10.1016/j.gca.2021.01.003.

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