Title: A two-year automated dripwater chemistry study in a remote cave in the tropical south Pacific: Using [Cl⁻] as a conservative tracer for seasalt contribution of major cations

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Abstract

Stalagmite Mg/Ca and Sr/Ca ratios are commonly interpreted as proxies for past hydrologic conditions and are often used to supplement carbon and oxygen stable isotope records. While the processes that control these element ratios, including water-rock interaction, dripwater residence time, and upstream precipitation of calcite, are well understood in continental caves, there have been few investigations of dripwater Element/Ca (X/Ca) evolution in coastal marine caves where seasalt can have a strong influence on the incoming Mg/Ca ratio.

We instrumented a marine cave on the remote South Pacific island of Niue to record daily cave microclimate, as well as weekly-integrated drip rates, dripwater oxygen and hydrogen isotopes, and dripwater chemistry over a period of twenty-two months. Using chloride as a conservative tracer for sea-spray, we calculate that seasalt input accounts for a large portion of dripwater Na, SO₄, and Mg (89, 93, and 85% respectively) and a smaller portion of the Ca and Sr (19 and 17%). During the second year of this study a gradual decrease (by ~18%) in dripwater chlorinity was observed, suggesting that an epikarst-hosted seasalt aerosol inventory was being diluted over time. Minor element to calcium ratios for B, K, Cl, SO₄, Mg, Na, Sr, and Fe all strongly covary over the observation period, suggesting that although sea-spray plays a significant role in modulating incoming drip chemistry, prior calcite precipitation (PCP) dominates chemical evolution within the epikarst. During a prolonged drought episode, evaporative enrichments in dripwater δD and $\delta^{18}O$ (+4‰ and 0.5‰, respectively) were observed to coincide with increased cation and anion concentrations, strong Ca removal via PCP, and increases in Sr/Ca and Mg/Ca ratios (28% and 34%, respectively), suggesting that concomitant enrichment in speleothem $\delta^{18}O$ and X/Ca ratios may be interpreted as multi-proxy evidence for dry climate conditions.

We use modern dripwater chemistry and empirical water-calcite distribution coefficients to predict a range of stalagmite X/Ca ratios. We then forward model a number of scenarios that could modulate stalagmite chemistry, including increased/decreased seasalt input and changing dripwater flow path through calcite, dolomite, and aragonite bedrock. One major implication from this study is that even if PCP and flow path lithology remain constant over time, changing seasalt input can drive stalagmite Mg/Ca and Sr/Ca ratios away from PCP-controlled covariation, and lead to strongly varying Sr/Mg ratios. Thus in order to interpret coastal cave stalagmite X/Ca records accurately, it is necessary to estimate seasalt input and analyze parent drip and bedrock chemistry to quantify the influence of each contributing process.

1. Introduction

Stalagmites are useful archives for stable isotope and trace element climate proxies. Oxygen isotopes ($\delta^{18}\text{O}$) are the most widely used climate proxy in stalagmites, but when examined in isolation it is difficult to separate the effects of competing processes that fractionate oxygen isotopes, including changes in cloud temperature, rainfall amount, moisture source, and mineral precipitation temperature (McDermott, 2004; Lachniet, 2009). Other proxies such as carbon isotopes ($\delta^{13}\text{C}$) and minor element to calcium ratios (X/Ca) may be examined in conjunction with $\delta^{18}\text{O}$ in an effort to separate external climate signals from *in situ* processes (Treble et al., 2003; Johnson et al., 2006; Cruz et al., 2007; Baldini et al., 2015).

Minor element incorporation into stalagmite fabric was demonstrated by Fairchild et al. (2000) to be influenced by several processes, including leaching of cations from carbonate bedrock, incongruent dissolution of Mg and Sr-bearing dolomites, and prior-calcite-precipitation (PCP) within void spaces in the epikarst or on the cave ceiling. More recent investigations have

refined their interpretations through both mathematical models (Sinclair, 2011) and by controlled glass plate laboratory precipitation experiments (Day and Henderson, 2013). The ratios Mg/Ca and Sr/Ca are well understood in continental caves, and provide information about wet-vs-dry hydrologic conditions within the epikarst (Tremaine and Froelich, 2013), the strength and timing of cave ventilation (Wong et al., 2011), and evapotranspiration above the cave in arid climates (Rutledge et al., 2014).

Although dripwaters have been studied extensively in continental caves, there are few detailed investigations of maritime caves where dripwater X/Ca ratios may be influenced by seaspray (for example, see discussion in Fairchild et al., 2000; Baker et al., 2000, Moreno et al., 2010). Maritime caves may be subject to increased seasalt from rainfall, breaking waves (wet and dry aerosol), and extreme storm events (e.g., typhoons and hurricanes) that have the potential to add substantial quantities of seasalt ions to the epikarst and may lead to precipitation of evaporite minerals during dry periods. This additional source of ions to the epikarst increases the complexity of interpreting maritime stalagmite records because seawater and seasalt X/Ca ratios are very different from those of carbonate bedrock. Furthermore, seasalt input can change over time, potentially making it more difficult to separate in-cave processes from external climate forcing in the stalagmite minor element record.

Here we present results from a novel two-year (April 2012 through January 2014) automated dripwater monitoring program in a remote cave on the Island of Niue in the tropical south Pacific. High resolution cave monitoring traditionally requires frequent site visits; monitoring this remote location required the development of new sampling strategies. The cave was instrumented for continuous measurement of air temperature (T), relative humidity (RH), and pCO₂. A drip site corresponding to a long stalagmite record was monitored for flow rate,

dripwater $\delta^{18}\text{O}$ and δD , and dripwater cations (B, Na, Mg, K, Ca, Fe, Sr) and anions (F, Cl, Br, SO_4). In addition, ambient atmosphere immediately outside the cave was monitored for T and RH.

We use $[\text{Cl}^-]$ as a conservative tracer for seaspray input to investigate the hypothesis that seasalt aerosols influence cave dripwater and thus stalagmite geochemistry, complicating the climate record left by the rainfall-driven terrestrial processes of *in situ* bedrock dissolution and PCP. Depending on the magnitude of variability in seasalt addition over geologic time, Mg/Ca and Sr/Ca ratios could decouple and diverge away from the PCP signal which is characterized by near-constant Sr/Mg ratios (Tremaine and Froelich, 2013) with a $\ln(\text{Sr}/\text{Ca})$ vs. $\ln(\text{Mg}/\text{Ca})$ slope of $\sim 0.88 \pm 0.13$ (Sinclair, 2011). Previous analyses of Niue stalagmites demonstrated a series of abrupt increases in Mg, Na, P, and S that were attributed to landfall of tropical cyclones on the leeward side of the island (Murgulet and Aharon, 2006; Murgulet, 2010). More recently, Baldini et al. (2015) used dripwater cations in a cave in NW Spain as a tracer for variations in storminess and seaspray input to the karst terrain. They demonstrate that stalagmite Mg content is a result of more/less Mg seasalt aerosol as a function of the strength and latitudinal location of North Atlantic westerly winds during the Younger Dryas event. Thus the goals of this study are to (1) identify and quantify the primary controls on major ion concentrations in dripwater with respect to surface meteorological processes on Niue Island, (2) determine a baseline annual range in modern dripwater chemistry, and (3) apply this modern calibration to the interpretation of stalagmite climate records from Niue caves currently being generated by our group.

2. Site Description

Niue Island is a carbonate platform occupying 260 km² in the central south Pacific (19° 3'27.49"S; 169°51'30.60"W), within the South Pacific Convergence Zone (SPCZ) (Fig. 1a). The SPCZ is the largest rain band in the southern hemisphere and is largely controlled by oscillations in sea surface temperature (Widlansky et al., 2012). Thus, rainfall at Niue is seasonal and is affected by variations in the strength of the El Niño Southern Oscillation (ENSO). Average monthly summer “wet” season (November through March) precipitation during the two year period of this study was 283 ± 166 mm, and winter “dry” season (April through October) monthly precipitation was 112 ± 76 mm (Fig. 1b), while summer and winter air temperatures averaged 27.4 ± 0.5 °C and 25.4 ± 1.2 °C, respectively.

Niue is covered by thin (~30 cm; Aharon et al., 2006) lateritic soils characterized as inceptisols, mollisols, and oxisols that obscure irregular surface bedrock comprising pinnacled coral and dolomite. Soil mineral content consists primarily of gibbsite, goethite, crandallite, and boehmite (Whitehead et al., 1993). Wheeler et al. (1999) summarized Niue dolomite textures and geochemistry: upper dolomites (-20 to +40 meters above sea level) are calcian to stoichiometric, with major element composition ranging from 40.2 – 46.7 Mg mole %, 93 – 286 ppm Sr, and 144 – 462 ppm Na (n=91) (Table A1). Dolomite δ¹³C ranges from +1.5 to +3.3‰ (PDB), and δ¹⁸O ranges from +1.2 to +4.3‰ (PDB). Isolated calcite and aragonite beds were observed, but evaporite beds were absent in their core measurements.

Located in the northwest part of the island near the popular tourist formation known as ‘Talava Arches’, the cave formed within a tall, narrow, approximately E-W trending fissure in the ~ 30 m high limestone cliffs that make up the perimeter of the island. The roof of the cave is sealed and the entrance is partially closed by collapsed rubble and old flowstone. The floor of the

cave in many places is intact reef-terrace raised approximately 2 meters above modern sea level. Airflow into the cave is restricted by the narrow entrance and by several crawl-height passages within. Weak fluctuating ventilation is evident and atmospheric pCO₂ levels measured in the deep interior varied between 395 ppm (atmospheric) and ~1000 ppm. Observed throughflow of air indicates that the cave may open out to the surface, a hypothesis supported by the presence of tree roots and some soil staining in the higher reaches of the cave. However, it is likely that surface connections are small given the weakness of airflow through the cave.

Active speleothem formations are present within the cave, including wall flowstone, stalagmites, stalactites, (including numerous long soda-straws), ribbons, wide columns, rimstone pools, and helectites. Some of these clearly form along cracks, but the roof is extensively decorated except where recent breakdown has occurred. Rubble (both fresh and cemented) is common throughout, as expected for a cave in a tectonically active region where island uplift is 0.13 – 0.16 mm yr⁻¹ (Terry and Nunn, 2003). Breakdown tends to make large stalagmites rare, but a number of 50 – 100 cm stalagmites are found in more stable parts of the cave. An 83,000 year-old stalagmite (TA-01), is currently being analyzed by our group for paleoclimate reconstruction (discussed in a forthcoming publication). Stalagmite TA-01 was taken from among a gallery of stalagmites and columns in an enlarged chamber about 100 meters from the restriction point that marks the beginning of the cave (Fig 1).

3. Methods

Dripwater was collected from the stalactite that was feeding Stalagmite TA-01. The stalactite resides approximately 2.5 meters above the local cave floor and is about 10 cm long. Dripwater appeared to be flowing through the inside of the stalactite rather than down the outside. Weekly

dripwater samples were collected using a custom-built battery powered carousel-style autosampler which caught drips in a funnel and distributed them sequentially to an array of twenty-four 120 mL acid-washed (HNO_3) glass bottles fitted with lids with a round hole in the center (Fig. 2). Sample bottles were pre-filled with 10 mL of mineral oil to act as a floating seal to prevent evaporation, and also to limit degassing and precipitation of CaCO_3 in the sample bottles. Bottles were collected approximately every five months, and samples were not acidified in the field. Bottles were capped tightly (Teflon seal), further sealed with electrical tape and refrigerated in the dark prior to transport back to Rutgers University for subsampling and analysis. It is possible that some degassing may have occurred during deployment, however precipitates were not observed in dripwater samples.

Overflow of the mineral oil was prevented by a small hollow polypropylene ball floating on top of the oil layer, which sealed against the hole in the bottle cap when the bottle was full (Fig. 2). When this occurred during a sample collection interval, further drips ran down the outside of the bottle and were collected (for volume estimate, not for chemical analysis) in a plastic bag surrounding the bottle. This overflow water was measured in the cave using a 100 mL graduated measuring cylinder. Because there was no access to a precision balance in the field, the volume of water in each bottle was estimated by measuring its height (bottles had been previously calibrated using the graduated cylinder). Uncertainty for this volume-estimation technique was +/- 2 mL, based on replicate measurement of known volumes.

Daily rainfall amount, temperature, relative humidity, wind speed and wind direction from 2011 through 2014 were measured at the Niue International Airport approximately 14 km south of the study site (data provided by the Niue Meteorological Office). We calculate net rainfall

(NR) as weekly precipitation minus weekly apparent evapotranspiration using the “Thorntwaite” equation after Willmott et al. (1985) (Eq. 1 - 4):

$$I = [T_i / 5]^{1.1514} \quad (1)$$

$$\alpha = [6.7 \times 10^{-7} I^3] - [7.7 \times 10^{-5} I^2] + [1.79 \times 10^{-2} I] + 0.49 \quad (2)$$

$$\text{Potential Evapotranspiration (PE)} = (16 \times [10 \times T_i / I]^\alpha) \times [7/d] \quad (3)$$

$$\text{Apparent Potential Evapotranspiration (APE)} = \text{PE} \times [d/30] \times [h/12] \quad (4)$$

where T_i is monthly mean temperature, I is the heat index, α is a multiplicative of the heat index, d is days in each month, and h is hours of sunlight on the 15th day of each month.

In March 2012 a Vaisala GMM222 CO₂ sensor (Vaisala, Helsinki, Finland) attached to a HOBO H21-002 data logger (Onset, MA, USA) was installed adjacent to the drip site. Since there were no feasible direct power options, instruments were powered by six EvereadyTM 1409 6V batteries wired as two banks of three in parallel to provide 30 amp hour capacity at 12V. To conserve battery power, a programmable timer was set up to turn the CO₂ sensor on for 20 minutes at 6 am and 6 pm each day. Readings were averaged over 20 minutes and the unit was switched off again. This allowed weekly fluctuations in CO₂ to be resolved across the ~6-month intervals between field trips. During field trips, the sensor was switched to take one measurement every three hours allowing diurnal variations to be studied.

3.1 Analysis of Dripwater $\delta^{18}\text{O}$ and δD

Subsamples were pipetted from sample bottles in the lab, then analyzed using a Picarro L2130-i Cavity Ring-down Spectroscope (CRDS) connected to a Picarro high-precision A0211 vaporizer (140 °C) coupled with a HTC-xt Leap Pal Tech auto sampler at the Lamont-Doherty Earth Observatory following the methods outlined in Friedrich and Schlosser (2015a, 2015b). Samples were injected using clean 10 μL syringes to perform within instrumentation

requirements (19,000 – 21,000 ppmv). The reported value for each sample is the average of the last three out of six injections. The data were calibrated based on measurements of interspersed sets of two certified standards and three in-house standards (Table A2). Samples are reported as δD and $\delta^{18}O$ referenced to the international VSMOW-Standard Light Antarctic Precipitation (SLAP) scale. Calibration curves were anchored by GISP ($\delta D = -189.5 \pm 1.3\text{‰}$, $\delta^{18}O = -24.78 \pm 0.15\text{‰}$ VSMOW-SLAP) and VSMOW2 ($\delta D = 0.0 \pm 0.3\text{‰}$, $\delta^{18}O = 0.00 \pm 0.02\text{‰}$ VSMOW-SLAP). The long-term reproducibility of this method is 0.05‰ or better for $\delta^{18}O$ and 0.5‰ for δD .

3.2 Analysis of Dripwater Cations and Anions

Subsamples of dripwater anion (Cl^- , F^- , SO_4^{2-} , Br^-) samples were diluted to approximately 23 mmol L⁻¹ [Cl^-] by pipetting 1.33 mL of sample into 3.64 mL 18.2 MΩ•cm MilliQ™ deionized water, then analyzed on a Dionex ICS-1000 Ion Chromatograph (IC) in the Department of Environmental Sciences, Rutgers University. Calibrations were performed at the beginning and end of each run using in-house IC check standards prepared from serial dilutions of 1000 mg L⁻¹ multi-element primary standards. Analytical uncertainties (1σ-RSD) determined from multiple analyses of in-run check standards were 0.30% for [Cl^-], 3.5% for [Br^-], 2.6% for [SO_4^{2-}], and 6.9% for [F^-]. Fluoride was below detection limits for nearly all samples and will not be discussed further. See Table A3 for standard concentrations.

Unfiltered samples for minor element analysis, largely cations (Ca, Mg, Sr, Fe, B, K, S, and Na), were diluted to approximately 2 mmol L⁻¹ [Ca] in 2% Optima™ (Fisher) ultrapure HNO₃. Samples were analyzed on a Varian™ Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) at the Department of Marine and Coastal Sciences, Rutgers University. Analyses were performed using a standard-sample-standard bracketing technique every five

samples with in-house standards prepared from serial dilutions of Alfa Aesar™ high-purity primary standards. Certified check standards (SLRS-5, SRM-1640, SRM-1643, CASS-5, and NASS-5) were interspersed at regular intervals during each run. Long-term analytical precision was typically less than 5% RSD. Calibration standard values are given in Table A3.

4. Results

4.1 Niue Rainfall Amount and Dripwater δD and $\delta^{18}O$

Niue dripwater δD and $\delta^{18}O$ plot along a line with the regression $\delta D = (7.8)\delta^{18}O + 9.6\text{‰}$; the slope of which is nearly identical to that of the global meteoric water line (GMWL: $\delta D = (8.0)\delta^{18}O + 10\text{‰}$; Craig, 1961) and the South Pacific Meteoric Water Line derived from rainfall data of Samoa and Rarotonga (SPMWL: $\delta D = (7.7)\delta^{18}O + 9.3\text{‰}$; Aharon et al., 2006) (Fig. 3). The slope of the dripwater line is affected by approximately fifteen samples that were collected during a prolonged drought episode between June and October 2012. The total range in dripwater isotopes is very small in comparison to the wide range in meteoric precipitation reported for this region of the South Pacific (ranges $\sim 55.5\text{‰}$ and 9.69‰ for δD and $\delta^{18}O$, respectively; GNIP – Rarotonga Station 1957-1994). Such a small range in dripwater is typically attributed to multi-rainfall mixing of meteoric waters within the soil and epikarst reservoir such that the isotopic signal of dripwater is buffered compared to the larger isotopic variation of individual rainfall events (Moerman et al., 2014), however reduced seasonality could also occur if recharge was highly biased toward one season or type of event (e.g., large rainfall events).

Taken as a whole, dripwater isotopes exhibit no seasonal difference in absolute values. Winter dry season $\delta^{18}O$ averaged $-4.70 \pm 0.13\text{‰}$ and δD averaged $-27.10 \pm 0.97\text{‰}$, while during the summer wet seasons $\delta^{18}O$ averaged $-4.75 \pm 0.06\text{‰}$ and δD averaged $-27.42 \pm 0.58\text{‰}$ (Fig. 4).

However, these averages are skewed by the fact that the collection carousel malfunctioned and dripwaters were not collected between June and September 2013, normally the dry season. In the 17 months prior to this study (Jan. 2011 through Apr. 2012), Niue net rainfall (NR = measured precipitation minus apparent evapotranspiration; see electronic annex Table 5 for calculations) averaged +113 mm month⁻¹. During this study (April 2012 through March 2014) Niue NR averaged only +9 mm month⁻¹ (Fig. 4), due in part to the fact that the 2012-13 summer was anomalously dry, averaging just +78 mm month⁻¹ compared to +235 mm month⁻¹ during the previous summer. During the drought episode between June and October 2012, dripwater δD and $\delta^{18}O$ became significantly more enriched than the arithmetic averages for the entire study period (Fig. 4). At the beginning of the 2012-2013 wet season, isotopic values began to exhibit depletion that was rapidly reversed at the onset of the 2013 dry season. After the carousel was repaired, isotopic values remained relatively depleted for the remainder of the study, most likely due to an anomalously rainy dry season in 2013 when nearly 300 mm of rainfall was recorded during July (Fig. 4).

4.2 Dripwater Cations and Anions

Niue Cave dripwater molar Na/Cl ratios ranged from 0.872 to 1.098, with an average molar ratio of 0.97 ± 0.05 (1 SD, n=89). Between April and September 2012, dripwater Cl, Na, and Sr concentrations were flat, while Mg and S concentrations trended downward and Ca concentrations trended upward (Fig. 4). Limited rainfall in August and September coincided with a two-month peak in all element concentrations. After this peak, Cl, Na, Mg, Sr, and Ca concentrations trended downward for the remainder of the study. Sulfate concentrations trended downward for several months but increased at the end of the 2013 dry season. An overall 18%

reduction in dripwater chlorinity was observed between April 2012 and January 2014 (Fig. 4; panel C).

Similar to the approach of Fairchild et al. (2000) and Tremaine and Froelich (2013), we use chloride as a conservative and unique tracer of seasalt input to the karst aquifer supplying Niue cave, assuming negligible chloride is derived from bedrock (Kitano et al., 1975). We assume that seawater-derived ions are delivered to the dripwater source at the ratios in which they exist in mean seawater and that is that there is no fractionation of seawater ions from the seawater source to the cave dripwater. This assumption implies that no evaporite sequence of seasalt-derived minerals has formed or subsequently undergone incongruent weathering. Seawater contributions are calculated by (Eq. 5):

$$\%_{SW} = 100 - \left[\frac{X_{SW} - \left(\frac{X_{SW}}{Cl_{SW}} \right) \times Cl_{DW}}{X_{DW}} \right] \times 100 \quad (5)$$

where SW indicates seawater and DW indicates drip water. All dripwater X/Cl ratios plot above respective seawater ratios, indicating that seawater is not the sole source of Na, SO₄, Mg, Sr, K, and Ca (Fig. 5). We find that average SW contributions range from 0.0002% for Fe; 16 - 20% for Sr and Ca; 50 - 71% for B and K; 85% for Mg; 89% for Na and Br; and 93% for SO₄ (Table 1).

5. Discussion

The ultimate goal of calibrating modern cave conditions is to understand 1) how dripwaters acquire major ion and isotopic composition, and 2) how these signals are transferred into stalagmites, so that stalagmite chemical records can be used to reconstruct environmental conditions in the past. In section 5.1 we examine how evaporation within the epikarst affects

dripwater isotope and ion composition. In section 5.2 we discuss modern sources of ions to constrain potential contribution pathways. In section 5.3 we consider how PCP affects modern hydrochemical evolution. In section 5.4 we use modern dripwater chemistry and inorganic distribution coefficients to calculate a potential range for modern stalagmite chemical composition. In sections 5.5 and 5.6 we examine how long-term changes in seasalt input and drip flow paths might overwhelm the magnitude of prevailing *in situ* control of PCP, and thus require a different interpretation in the stalagmite record. Finally, in section 5.7 we summarize the magnitude of potential changes in stalagmite Sr and Mg and propose a strategy for teasing apart competing processes influencing the stalagmite paleoclimate record.

5.1 Identifying Evaporation Artifacts

The slope of the dripwater δD vs $\delta^{18}O$ regression is approximately 7.8 (Fig. 3), which is expected given that the slope of the GMWL is 8.0 and the LMWL is 7.7 (Aharon et al., 2006). The slope of the line is anchored by several enriched dripwaters that were sampled during a prolonged drought, thus a likely source of enrichment is evaporation within the epikarst. Evaporation in an open system that is in contact with a low ambient humidity atmosphere, such as a lake surface or dry and well ventilated epikarst, is typically a kinetic process that promotes Rayleigh-type fractionation and results in δD vs. $\delta^{18}O$ slopes that range from 3.9 (RH = 0%) to 6.8 (RH = 95%) (Gat and Gonfiantini, 1981; Sharp, 2007). Such is sometimes the case for cave dripwaters in semi-arid environments (e.g., Cuthbert et al., 2014). But under closed-system, wetted epikarst conditions where evaporation is only slightly greater than condensation (RH > 95%), the reservoir can undergo near-equilibrium evaporation, resulting in a slight enrichment as light isotopes preferentially escape with the vapor through cracks in the epikarst while the bulk

condensate remains in contact with the original reservoir (Gonfiantini, 1986; Cuthbert et al., 2014).

To estimate the evaporation volume necessary to drive the maximum observed isotopic excursion of approximately +4.1‰ (δD , during dry period of 2012; Fig. 4b) above the arithmetic mean of all data (dashed line in Fig. 4b), we use a generalized mass balance approach expressed as:

$$\delta_l = [\alpha \delta_{tot} + 1000F(\alpha - 1)] / [\alpha(1 - F) + F] \quad (6)$$

$$\delta_v = \delta_l - 1000(\alpha - 1) \quad (7)$$

Where δ_l is the delta value of hydrogen isotopes in the condensate liquid, δ_v is the delta value of the vapor (-87.93), δ_{tot} is the delta value for the total reservoir (average $\delta D = -27.1$ ‰ in July 2012, Fig. 4b), α is the liquid-vapor fractionation factor for hydrogen isotopes at 30°C (1.07212; Kakiuchi and Matsuo, 1979), and F is the fraction of the reservoir lost as vapor.

We assume that the enriched condensate liquid ($\delta D = -23$ ‰ in Oct. 2012, Fig. 4b) is well mixed with the bulk reservoir and calculate that the total volume of evaporation required to drive this +4.1‰ excursion in δD during the 2012 drought episode is 17.2% of the initial reservoir volume. This evaporation would also act to concentrate aqueous ions by 17.2%, driving an increase in Cl, Na, Mg, SO_4 , Ca, and Sr of 3933, 3815, 431, 215, 379, and 3.7 $\mu mol L^{-1}$, respectively.

For Cl, Na, Mg, and SO_4 these estimates are slightly higher than the sudden increase in ion concentrations observed in September 2012 just before the drought ended and the reservoir was refilled with fresh rainfall (Fig. 4). For Ca and Sr, these estimates may not be applicable because Ca and Sr are bedrock-derived and the evaporation affecting the other ions is taking place in the wetted soil zone. As with most systems, equilibrium evaporation was not entirely achieved. It is

likely that the liquid-vapor fractionation factor that we used overestimates the degree of equilibrium maintained during evaporation and that evaporation volume may have been lower. It is also possible that fresh rainwater partially diluted the epikarst reservoir during the drought period. In either scenario it is clear that near-equilibrium evaporation caused an increase in cation and anion concentrations during the 2012 drought. Significant reservoir recharge was observed in DJF 2013, coinciding with dripwater isotopes that dipped below the dripwater $\delta^{18}\text{O}$ and δD average (dashed line, Fig. 4b) and the beginning of a slow but steady decline in total ion concentrations (Fig. 4c-e). A strong enrichment of dripwater isotopes was again observed at the onset of the 2013 dry season (Fig. 4b). Ion behaviors during the 2013 dry season may have resembled those in the last half of the 2012 drought, however dripwater data was not obtained during this time period. Dripwaters were not observed to reach the calculated volume weighted mean rainfall isotopic composition for Rarotonga (black dotted line Fig. 4b), the closest location with a multi-year rainfall amount and isotope record, suggesting that all Niue dripwaters are subject to some evaporative enrichment.

5.2 Identifying Ion Sources

Dripwater ions at Niue may be sourced from aqueous transport of dissolved carbonate bedrock and associated minerals within the epikarst and dissolution of evaporite sequences above the cave. Unlike inland caves far from the coast, sources of ions at Niue may also include modern sea-spray aerosols delivered by meteoric deposition to the epikarst. In the following, we consider each route.

Aerosol delivery: Niue dripwaters contain $19 - 27 \text{ mmol L}^{-1} [\text{Cl}]$, whereas inland cave waters contain about two orders of magnitude lower $[\text{Cl}]$ (0.29 mmol L^{-1} , Clamouse Cave, Fairchild et al., 2000; 0.27 mmol L^{-1} , Wollondilly Cave, McDonald et al., 2007; 0.48 mmol L^{-1} , Bunker

Cave, Reichelmann et al., 2011; 0.25 mmol L⁻¹; Hollow Ridge Cave, Tremaine and Froelich, 2013). Tsyro et al. (2011) demonstrate that marine aerosol contributions to meteoric water are dependent on wind speed. Baldini et al. (2015) therefore argued that stalagmite Mg concentrations increase with increasing strength of westerly winds near the northern coast of Spain. Increased wind speeds at Niue should enhance incorporation of sea-spray into the marine boundary layer, resulting in higher Cl deposition during windier months. Since wind speeds are seasonally cyclical at Niue (see Fig. A1), we would expect that Cl deposition (and thus dripwater [Cl]) should also exhibit seasonal variations. However, dripwater Cl is observed to be stable and relatively high from April through August 2012 at about 23 mmol L⁻¹, then to abruptly increase to nearly 25 mmol L⁻¹ in September before decreasing steadily by approximately 18% over the following 16 months (Fig. 4d). This behavior coupled with the muted range in dripwater isotopes that suggests multi-month residence time renders us unable to validate the premise that seasonal winds deliver a varying flux of seasalt aerosols to the soil surface. Alternatively, Murgulet and Aharon (2006) argue that abrupt increases in stalagmite Mg, Na, S, and P result from cyclone-driven deposition of bulk seawater over cliff walls and onto the soil above Niue caves. The steady washout of Cl observed between October 2013 and March 2014 may represent long-term recovery from ionic inputs during a previous cyclone (e.g., Category 5 Cyclone Heta, February 2004), and suggests that the soil seasalt inventory is large relative to subsequent windy season aerosol inputs. Although wind speed may be a contributing factor for aerosol delivery to the soil zone, the apparent karst water residence time prevents inference of seasonal to annual scale aerosol inputs from dripwater chemistry.

Bedrock dissolution: Niue is a former aragonitic reef complex that has been dolomitized under normal seawater conditions (Aharon et al., 2006). In addition to aragonite and dolomite, which

contain Sr in higher concentrations than in calcite, there also exist sporadic preserved beds of low-Sr calcite. According to the analyses of Wheeler et al. (1999), whole rock (congruent) dissolution of the upper dolomites should result in a dripwater solution composition that is 55 mol% Ca, 45 mol% Mg, 124-234 ppm Sr, and 241-386 ppm Na. It is very likely that the Ca, Mg, Sr, and Na that is not supplied by meteoric input of seasalts is derived from one or several of these bedrock carbonate phases.

Evaporite sequences: Wheeler et al. (1999) analyzed five cores from various locations across Niue, three of which were from the upper 50 meters of bedrock. The lithofacies of these cores were determined to be coral skeletal grainstone, packstone, and wackestone, geochemically comprising primarily dolomite, with less than 20% calcite and sporadic (<5%) aragonite. This study emphasized that evaporite sequences are absent. Later investigations of dripwaters from Niue caves revealed that dripwater [Na] and [Cl] were up to eight times more concentrated than in freshwater-lens groundwaters (Aharon et al., 2006) and that dripwater Na/Cl molar ratios (1.03 to 1.46) were notably greater than that of seawater (0.86). Aharon et al. (2006) posited that in order for dripwater Na/Cl to exceed that of seawater, there must exist a pure source of NaCl, and therefore rainwater must percolate through an epikarst containing halite (NaCl) grains. Dripwater molar Na/Cl ratios in this study are 0.97 ± 0.05 (1σ), also suggestive of disseminated halite. However, if halite were the sole source of dripwater Na, then other ions such as Mg and SO_4 would not correlate well with Cl, as observed (Fig. 5). Additional evidence against halite dissolution as a dominant mechanism is observed during two episodes where Na decouples from Cl (J-F and O-D 2013; Fig. 4c). We argue that seasalt aerosol delivery to the epikarst accounts for all Cl, and about 89% of the Na. The remainder of the Na in solution is likely sourced from dissolved bedrock, where Na ranges from 241-386 ppm (Wheeler et al., 1999).

5.3 Identifying Prior Calcite Precipitation

Incoming dripwater chemistry is set by a combination of the composition of meteoric waters, dissolved carbonate bedrock, soluble soil minerals, and degree of evapotranspiration. When dripwater reaches void spaces within the epikarst (or the main cave chamber itself), degassing of CO₂ drives the water to supersaturation ($\Omega \geq 1$) with respect to calcite, and then Ca is removed from solution by precipitation of calcite via PCP (Pilson, 1998; Fairchild et al., 2000). As PCP proceeds, other minor elements such as Mg and Sr are continually enriched in the residual solution because their solid-solution distribution coefficients [$D_x = (X/Ca)_{\text{calcite}}/(X/Ca)_{\text{H}_2\text{O}}$] (Henderson and Craček, 1927) are less than 1.0. Under the condition that initial dripwater composition remains constant (no changes in seasalt input or dripwater flow paths through different lithology), PCP drives co-varying increases in Mg/Ca and Sr/Ca ratios in an approximately straight-line relationship governed by their distribution coefficients (Eq. 8) (Tremaine and Froelich, 2013; developed from equations in Fairchild and Baker, 2012):

$$\frac{Sr}{Mg} = \frac{Sr_o - \Delta Ca(D_{Sr})}{Mg_o - \Delta Ca(D_{Mg})} \quad (8)$$

where Sr_o and Mg_o are the initial dripwater Sr and Mg concentrations, and ΔCa is the molar removal (precipitation) term. When PCP extent is the driving mechanism, X/Ca ratios in dripwater time series tend to covary because Ca removal dominates the signal.

As a test for the strength of PCP as a modulating factor in dripwater chemistry, X/Ca ratios are plotted against Mg/Ca ratios (Fig. 6). The Sr/Ca vs. Mg/Ca regression trends along a modeled PCP vector, from low PCP plotting near the unmodified groundwater endmember (gray area, Fig. 6f), to high PCP conditions that extend toward the distal end of the PCP vector. Similarly, Fe, SO₄, B, Na, and K trend along lines of nearly-constant X/Mg ratio, indicating that each of these elements is strongly controlled by upstream PCP as the common denominator (Ca) is

removed from solution. Since D_{Fe} and D_B are both greater than unity, it is expected that their ratios to Ca should be decreasing in the dripwater during PCP if they are being incorporated into the $CaCO_3$ mineral. Thus we infer that they are associated with suspended particulate or colloidal matter in the drip and their covarying X/Ca ratios are simply a result of Ca removal.

Dripwater chemistry evolves away from the initial solution composition during periods of increased PCP extent, which typically occurs in higher ventilation regimes (Wong et al., 2011) or during dry episodes (Partin et al., 2012; Tremaine and Froelich, 2013). Cave ventilation can be driven by density contrasts between atmospheric air and cave air that result in low pCO_2 (~395 ppmv) atmospheric air diluting high pCO_2 (500-20,000 ppmv) cave air (e.g., Spötl et al., 2005; Baldini et al., 2008; Kowalczyk and Froelich, 2010), or by atmospheric air becoming entrained into a cave entrance via heat exchange interaction with cave walls, also called chimney-ventilation (Matthey et al., 2010). Comparing the range in Niue Cave pCO_2 (395-800 ppmv; Fig. 7F) with that of other caves from different latitudes and altitudes (400-1,500; Obir Cave, Spötl et al., 2005; 400-1,700; Ballynamintra Cave, Baldini et al., 2008; 400-37,000; Natural Bridge Caverns, Wong et al., 2011; 409-3,565; Hollow Ridge Cave, Tremaine et al., 2011), it is evident that Niue Cave is strongly to moderately ventilated year round.

Niue Cave dripwater Mg/Ca and Sr/Ca ratios covary strongly with SO_4/Ca , Na/Ca , Fe/Ca , K/Ca , B/Ca , and Cl/Ca (Fig. 7), suggesting that even though seasalt contribution to Mg is relatively high in the incoming dripwater and evapotranspiration plays a large role in modulating soil and epikarst salt concentrations, PCP is the primary driver of hydrochemical evolution at this drip site. If ventilation rates were controlling degassing rates and thus the extent of PCP in the Niue cave, then X/Ca ratios should increase during the cool winter dry season when ventilation rates are higher, and decrease during the warm wet season when ventilation rates are slower.

However, the opposite is observed: dripwater X/Ca ratios decrease from April to November 2012 (low $p\text{CO}_2$), increase from November 2012 to June 2013 (high $p\text{CO}_2$), and remain high but variable after September 2013 (Fig. 7f). There is no relationship between strong ventilation and increased X/Ca ratios. Similarly, there is no observable relationship between drip rate and X/Ca ratios. This suggests that drip rate has little affect on PCP in this system (Fig. 7g). However, it has been shown that in regions with distinct wet and dry seasons, large rainfall events may induce a piston effect causing dripwater pulses containing higher total dissolved solids and X/Ca ratios due to the carry-through of long residence time water that has undergone CO_2 loss (Rutledge et al., 2014). This process complicates direct comparison of drip rates and X/Ca ratios on short time scales, as in this study. The lack of correlation between drip rate, ventilation and X/Ca suggests an alternative possibility, evaluated in the next section, that PCP is controlled by dripwater saturation state through the initial saturation of the dripwater in the soil zone, rather than by degree of disequilibrium with cave air $p\text{CO}_2$.

5.4 Establishing a Modern Baseline to Compare to Paleo Records

Variations in stalagmite Sr/Ca and Mg/Ca ratios are often interpreted as changes in hydrologic saturation of the epikarst, and thus climate induced changes in rainfall (e.g., Roberts et al., 1998; Treble et al., 2003; Johnson et al., 2006; Cruz et al., 2007). In this case, the mean value of dripwater X/Ca ratio is controlled by the concentration of Ca in the dripwater reservoir (which is a function of reservoir water residence time), while the absolute X/Ca ratio, varying about the mean, is a function of PCP intensity. Figure 4 shows that during the beginning of the drought episode in 2012, seasalt-derived ions such as Cl, Na, Mg, and SO_4 remained flat or decreased in concentration prior to the peak in September, while bedrock derived ions Ca and Sr increased during the drought when lack of rainfall resulted in increased reservoir residence time, increased

water-rock interaction, and increased dissolution of bedrock. These behaviors suggest that prior to the drought, the water reservoir was full and in continual contact with the soil (the main repository of seasalt aerosols). As drought conditions progressed, the reservoir lost volume via evaporation and dripping, moving downward away from the soil and concentrating seasalt ions. We infer that while [Ca] (and therefore dripwater saturation with respect to calcite; Ω) is affected by the length of time that the reservoir is in contact with bedrock (residence time), seasalt ion concentrations are affected by the duration of vertical contact between the water reservoir and the soil. During the evaporative peak in seasalt ions, a $595 \mu\text{mol L}^{-1}$ decrease in Ca is observed (Sept.-Oct., 2012; Fig. 4), suggesting a large increase in PCP and resultant X/Ca ratios (Fig. 7). As rainfall increased, residence times decreased and all ion concentrations followed suit until the beginning of the next dry period. The upward bow in the Ca curve (Fig. 4) during the drought has the effect of generating a downward bow in X/Ca ratios over the course of 2012 and early 2013 (Fig. 7).

Coupled with the behavior of dripwater isotopes, these results suggest two potential interpretations of Niue speleothem records: 1) During periods of abundant rainfall, annual-scale (or longer) stalagmite X/Ca ratios and $\delta^{18}\text{O}$ under this drip must be proxies for karst water residence time and overall wet-vs-dry atmospheric conditions, such that lower X/Ca ratios and depleted $\delta^{18}\text{O}$ are indicative of wet periods; and 2) During periods of prolonged multi-year drought, evaporation drives enrichment in dripwater (and thus speleothem) $\delta^{18}\text{O}$ and increases Ca removal via PCP, ultimately promoting increased X/Ca ratios (Fig. A2). Two endmember scenarios associated with these interpretations are posited but were not observed during this two-year period. The first would be extremely wet conditions that decrease residence time and increase drip rates such that PCP is effectively ‘turned off’, resulting in a very low dripwater

Sr/Ca ratio that matches dissolved bedrock. The second would be extremely dry conditions that would increase the extent of PCP, increasing X/Ca ratios to a maximum constrained by the drip becoming undersaturated with respect to CaCO_3 ($\Omega \leq 1$). Superimposed on these endmembers and the range of behaviors between them is the potential for variations in seasalt input. Speleothems in Niue cave grow at approximately $30\text{-}50 \mu\text{m yr}^{-1}$, providing annual to decadal resolution (Sinclair et al., 2014). Seasonal scale variations are not observable using conventional milling techniques.

Modern dripwater composition can be used to estimate a range of possible stalagmite compositions by applying known distribution coefficients (D_x ; see Table A5). The value of D_{Mg} is influenced by temperature (Oomori et al., 1987; Huang and Fairchild, 2001; Day and Henderson, 2013), while D_{Sr} is affected by stalagmite growth rates (Lorens, 1978; Baker et al., 1998; Banner et al., 2007). Both D_{Mg} and D_{Sr} can be affected by changes in mineralogy and crystal structure (Holland et al., 1963, 1964; Riechelmann et al., 2014). Although dripwater Mg concentration is high, there is no indication of mineralogical changes (i.e., calcite to aragonite) in Niue speleothems. Preliminary age models from several stalagmites indicate axial extension rates on the order of $30 \mu\text{m year}^{-1}$ (Sinclair et al., 2014), with homogenous growth structures that eliminate the need for growth rate corrections on D_{Sr} . Given the tropical location of Niue, it is unlikely that glacial-interglacial temperature shifts were sufficient to require correction. To support this assertion, we use the lab experiment results of Day and Henderson (2013) ($\Delta D_{\text{Mg}} \sim 2\% \text{ } ^\circ\text{C}^{-1}$) to calculate that a 5°C reduction in cave air temperature would prompt a $-1.8 \text{ mmol mol}^{-1}$ change in stalagmite Mg/Ca which is less than the $\sim 2.3 \text{ mmol mol}^{-1}$ change resulting from a 10% change in seasalt contribution (Table 2). This exercise illustrates that it would be difficult

to distinguish the effects of small changes in seasalt from large changes in temperature, as they affect the Mg/Ca record.

We can use the dripwater data to estimate the composition of a hypothetical stalagmite precipitating over the course of our observational period. Table A5 displays the average and 1-sigma variability of dripwater X/Ca ratios along with distribution coefficients and estimated stalagmite compositional ranges based on this modern day calibration study. Under modern conditions, mean dripwater Mg/Ca ($1243 \pm 221 \text{ mmol mol}^{-1}$, 1σ) and Sr/Ca ($10.7 \pm 1.8 \text{ mmol mol}^{-1}$, 1σ) (Sr/Mg = 0.00917) would result in a stalagmite with Mg/Ca and Sr/Ca of 38.5 ± 6.8 and 0.89 ± 0.15 , respectively. If sea-spray deposition were constant with time, there were no changes in drip flow path, and PCP were the primary *in situ* hydrochemical control, then the stalagmite should have a nearly constant Sr/Mg ratio of approximately 0.023 ± 0.003 . Analysis of stalagmite TA-01 is ongoing. Variations in Mg/Ca and Sr/Ca in the TA-01 record will be compared in a forthcoming paper to these modern predictions to estimate differences in dripwater composition between present and past and to posit mechanisms driving past X/Ca variations as related to paleo-climate in the region and globally.

5.5 Estimating Sensitivity to Changing Seasalt Input

When performing cave calibrations with the goal of applying modern dripwater chemistry to the interpretation of ancient stalagmite records, it is tempting to assume that cave conditions have been constant over long time scales. Two major caveats to such assumptions are: 1) In marine caves, seasalt input changes over time with wind speed, sea level, and likely other factors and 2) drip flow routes migrate through new mineralogy in soil and bedrock over time. Tremaine and Froelich (2013) proposed a rule that in order to interpret stalagmite Mg/Ca and Sr/Ca ratio time series as indicators of PCP conditions, it is critical that the Sr/Mg ratio is constant through

time. If flow routes change and access different bedrock mineralogies, then stalagmite Sr and Mg will become decoupled and the record will no longer solely represent PCP variations. This constant Sr/Mg rule is adequate for most inland caves, but is probably not an appropriate criterion for coastal caves because changes in seasalt input may also lead to decoupling between Mg and Sr, even when the drip has a constant flow path and *in situ* hydrochemical evolution is controlled by variations in the extent of PCP.

Modern dripwater chlorinity in the Niue cave represents very dilute seawater (23 mmol L⁻¹ vs. 559 mmol L⁻¹; about 4% of SW). A relative decrease of about 18% was observed during this short two-year study (Fig. 4), suggesting that it is unlikely that sea-spray deposition is constant on annual to decadal timescales through geologic time. To examine the potential impact of changing seaspray on stalagmite composition, we calculate dripwater and stalagmite Sr/Ca and Mg/Ca ratios in increasing and decreasing increments of 10% change in seasalt contribution relative to average concentrations from the 2-year study (Table 2). These calculations reveal that if seasalt input were reduced, dripwater would exhibit a large *decrease* in Mg/Ca and a slight *increase* in Sr/Ca because seasalt currently contributes 19% of Ca and 84% of Mg, but only 17% of Sr. As an example, the 18% reduction in dripwater chlorinity during this study manifested a measured increase in dripwater Sr/Mg from 0.0087 to 0.0093 (Fig. 7), in good agreement with our calculations.

A stalagmite forming from average modern waters would have a Sr/Mg ratio of 0.023. All things held equal, elimination of seasalt contributions would result in an increased stalagmite Sr/Mg ratio of 0.119, while a doubling of seasalt input (to ~ 8% seawater) would result in a decreased stalagmite Sr/Mg ratio to about 0.015. These ranges demonstrate that observations of long-term variations in stalagmite Sr/Ca and Mg/Ca that are coherent in timing and direction but

different in relative magnitude may be explained in part by changes in seasalt contribution. These changes would be especially evident in stalagmite Sr/Mg ratios.

5.6 Estimating Sensitivity to Changing Drip Flow Path

To examine the impacts of changing dripwater flow paths through different known carbonate minerals, we compare a modeled stalagmite formed from modern dripwater to three modeled stalagmites formed from dissolution of three distinct types of Niue dolomites previously characterized by texture (crystalline mimetic: CM; transitional crystalline mimetic-microsugrosic: CMS; and microsugrosic: MS; Wheeler et al. 1999). First, we subtract ions sourced from seasalt input to isolate the remaining ions contributed solely by dissolved bedrock (we explicitly assume congruent dissolution of bedrock) to arrive at a modern bedrock-derived drip composition of $\text{Mg/Ca} = 91.3 \text{ mmol mol}^{-1}$, $\text{Sr/Ca} = 4.03 \text{ mmol mol}^{-1}$ ($\text{Sr} = 3.52 \text{ ppm}$), and $\text{Na/Ca} = 459.9 \text{ mmol mol}^{-1}$ ($\text{Na} = 105 \text{ ppm}$). This exercise reveals that the drip is receiving ions from dissolved high-Mg calcite containing 1.5 – 2.5% of the Sr and 27 – 44% of the Na contained in Niue dolomites (Table 3, top panel).

Dolomites of types CS, CMS, and MS range from 41.4 – 44.9 mol% Mg and 142 – 234 ppm Sr (units after Wheeler et al., 1999). Stalagmites precipitating from dissolved calcite (without added seasalt) should have Sr/Mg ratios on the order of about 0.12, while stalagmites formed from dissolved dolomites should have Sr/Mg ratios ranging from 0.53 to 1.01 due to a 40 to 70 fold increase in dripwater Sr/Ca, and a 7 to 10 fold increase in dripwater Mg/Ca ratios (Table 3, top panel). Addition of modern levels of seasalt back into the dripwater results in stalagmite Sr/Mg that ranges from 0.022 (calcite) to 0.66 (dolomite).

This exercise demonstrates that the dramatic difference in bedrock Mg and Sr content provides a diagnostic indicator of changes in drip flow path through different mineralogy over

time. We calculate that stalagmites from Niue Cave may exhibit thirty-fold changes in Sr/Mg ratios as a function of variable mixing between high-Mg calcite and dolomite while holding seasalt input constant. Addition of seasalt higher than modern values would decrease these Sr/Mg ratios accordingly. Therefore, interpretation of paleoclimate records from Niue Cave stalagmites will require careful consideration of the complex results of variations in both seasalt input and source bedrock. These results are likely applicable to any marine cave that is subject to significant sources of sea-spray and is formed within interbedded dolomites, aragonites, and calcite limestones.

5.7 For the Record: Separating Competing Processes

We here attempt to identify and distinguish competing processes for a given period of interest within a Niue stalagmite record. We examine absolute Sr/Ca and Mg/Ca ratios with the understanding that strong modern PCP drives a 2-fold increase in modern Mg/Ca and Sr/Ca ratios as a function of the initial Ca concentration which is controlled by reservoir residence time, Ca saturation state, and overall hydrologic conditions (wet vs. dry). Resulting stalagmite Sr/Ca should range from ~ 0.7 to 1.1, while Mg/Ca should range from ~32 to 45 mmol mol⁻¹ (Table A5) while the Sr/Mg ratio should remain fixed at 0.023 mol mol⁻¹ (Table 2). For simplicity, these calculations do not take into account the seasonal shifts in Sr/Mg that would occur with variations in residence time (and associated bedrock dissolution) that would add slightly more or less Sr to the system. As shown in Table 2, variations in seasalt input from 20% lower to 40% higher than current values would generate a speleothem with Sr/Ca and Mg/Ca ratios that fall within this range, but would result in a shift in Sr/Mg from 0.027 to 0.019 mol mol⁻¹. Thus if variations in stalagmite Sr/Ca or Mg/Ca are examined in isolation, changes in seasalt within this range would be indistinguishable from the range produced by changes in

residence time. However, if Sr/Ca and Mg/Ca ratios are examined together such that the Sr/Mg ratio is the key parameter, *variations* in seasalt contributions can be accounted for and removed from the record so that X/Ca ratios may serve as true proxies for rainfall amount and associated hydrologic conditions in the epikarst.

Since increasing seasalt input can only lower the Sr/Mg ratio, changes in seasalt contribution are easily contrasted with changes in drip flow path through different bedrock mineralogy. For example, a shift in speleothem Sr/Mg above the modern zero-seasalt maximum of 0.126, would indicate that the drip must have migrated out of high-Mg calcite and into dolomite mineralogy where speleothem Sr/Mg ratios would be 0.362 - 0.656 (Table 3). This migration could take place very quickly (e.g., after seismic activity) or could progress steadily over long periods of time through a mineralogical assemblage such that Sr/Mg ratios vary continuously. These logical conditions can also be applied in the reverse direction.

6. Conclusions

Numerous recent studies have acknowledged the importance of *in situ* calibrations between modern cave conditions and several key influences on stalagmite geochemistry. This study demonstrates that:

- (1) While it is often logistically prohibitive to fully instrument remote locations such as Niue, novel low-power devices can enable collection of preliminary 'baseline' data sufficient to aid in interpretation of stalagmite records. Continued development of such devices is crucial to improved understanding of cave systematics in remote regions that are highly sensitive to climate change.

- (2) Using $[Cl^-]$ as a unique and conservative tracer of seasalt input to a coastal cave facilitates determination of the sources of climatically interesting ions such as Mg^{2+} , Sr^{2+} , K^+ , Na^+ , and SO_4^{2-} . This approach allows establishment of a modern baseline in dripwater Sr/Mg ratios and facilitates isolation and removal of a changing seasalt signal from variations in Sr/Ca and Mg/Ca that are driven by changes in rainfall amount and hydrologic saturation of the epikarst as a function of residence time and prior calcite precipitation (PCP).
- (3) We observe a linear decline in dripwater chlorinity during the second year of monitoring, suggesting that epikarst-hosted seasalt aerosols and halite minerals can build up during dry periods and get washed out during wet periods. This brief but significant excursion suggests that seasalt input to the cave dripwater is probably not constant with time.
- (4) Distinct lithological compositions above the Niue cave allow for analytical separation of climatically important variables such as variations in hydrologically-driven PCP and seasalt input from variations in dripwater flow paths that may confound paleorecords. Dripwaters during this twenty-two month study have covarying X/Ca ratios for all ions and are hydrochemically controlled by PCP. Stalagmite X/Ca records from Niue Cave may therefore be considered proxies for hydrology and climate when Sr/Mg ratios are constant, and proxies for flowpath variation and seasalt input when Sr/Mg ratios are strongly varying.
- (5) Niue Cave dripwater oxygen and hydrogen isotope ratio variations are muted with respect to variations in meteoric waters, indicating that water storage and mixing is sufficient to homogenize the incoming rainfall signal on seasonal timescales. Wet season dripwater isotopes are indistinguishable from the local meteoric water line suggesting that stalagmites from the Niue cave may be faithful proxies for local rainfall intensity and hydrologic conditions. During a prolonged drought episode, evapotranspiration coupled with zero

rainfall drove a 17% reduction in dripwater reservoir volume, causing near equilibrium evaporation-driven enrichments in δD (+ 4‰), $\delta^{18}O$ (+ 0.5‰) along the GMWL, and promoted Ca removal causing increased X/Ca ratios via PCP. These results provide strong evidence that concomitant increases in stalagmite X/Ca ratios and enrichments in $\delta^{18}O$ are associated with dry climate conditions.

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Tables

Table 1. Average seawater and Niue Cave dripwater composition. Seawater contributions to drip chemistry are calculated using chloride as a conservative tracer of seasalt input (see Eq. 5).

Element	Seawater ¹ mmol L ⁻¹	Ratio to Ca	Avg. Dripwater mmol L ⁻¹	Dripwater Range mmol L ⁻¹	Avg. SW Contribution %
Cl	559.4	53.3	21.377	18.68 - 26.7	100.0
SO ₄	28.9	2.8	1.192	1.09 - 1.4	92.7
Na	480.6	45.8	20.587	15.0 - 25.17	89.2
Br	0.87	0.082	0.037	0.022 - 0.078	89.3
Mg	54.1	5.2	2.446	2.3 - 2.8	84.5
K	10.5	1	0.563	0.37 - 0.78	71.0
B	0.42	0.040	0.0318	0.028 - 0.047	50.0
Ca	10.5	1	2.063	1.4 - 5.5	19.4
Sr	0.0928	0.0088	0.0213	0.016 - 0.023	16.6
Ba ⁽²⁾	0.000036	0.0000034	0.000057	0.000016 - 0.00039	2.4
Al ⁽⁴⁾	0.0000010	0.00000010	0.0036	0.002 - 0.04	0.0011
Fe ⁽³⁾	0.00000004	0.0000000038	0.00065	0.00057 - 0.00090	0.0002

¹ Pilson, M.Q. (1998)

² Dehairs et al. (1987)

³ Fitzsimmons et al. (2014)

⁴ Slemons et al. (2012)

Table 2. Arbitrary increase and decrease in seasalt contribution to current cave dripwater composition. Ca, Mg, Sr in mmol L⁻¹. Mg/Ca and Sr/Ca in mmol mol⁻¹. Assumed D_{Mg} = 0.031, and D_{Sr} = 0.083.

Seasalt		Dripwater					Speleothem		
Relative Change Amount %	Seawater %	[Ca] mmol L ⁻¹	[Mg] mmol L ⁻¹	[Sr] mmol L ⁻¹	Mg/Ca mmol mol ⁻¹	Sr/Ca mmol mol ⁻¹	Sr/Ca mmol mol ⁻¹	Mg/Ca mmol mol ⁻¹	Sr/Mg mol mol ⁻¹
100%	8.0	2.464	4.513	0.0248	1832	10.08	0.84	56.78	0.015
50%	6.0	2.264	3.480	0.0231	1537	10.19	0.85	47.65	0.018
40%	5.6	2.223	3.273	0.0227	1472	10.22	0.85	45.63	0.019
30%	5.2	2.183	3.066	0.0224	1404	10.24	0.85	43.53	0.020
20%	4.8	2.143	2.859	0.0220	1334	10.27	0.85	41.36	0.021
10%	4.4	2.103	2.653	0.0217	1261	10.30	0.85	39.10	0.022
Current Values	4.0	2.063	2.446	0.0213	1186	10.32	0.86	36.76	0.023
-10%	3.6	2.023	2.239	0.0209	1107	10.35	0.86	34.32	0.025
-20%	3.2	1.983	2.033	0.0206	1025	10.38	0.86	31.78	0.027
-30%	2.8	1.943	1.826	0.0202	940	10.42	0.86	29.14	0.030
-40%	2.4	1.903	1.619	0.0199	851	10.45	0.87	26.38	0.033
-50%	2.0	1.862	1.412	0.0195	758	10.48	0.87	23.51	0.037
-100%	0.0	1.662	0.379	0.0178	228	10.68	0.89	7.06	0.126

Table 3. **Top Panel:** Theoretical speleothem compositions based on dissolution of four known types of bedrock on Niue. High-Mg calcite values are estimated by subtracting the seasalt-derived portion of Ca, Mg, Sr, and Na from dripwater and assuming this composition represents pure dissolved bedrock (Table 1). Measured values for CM, MS, and CMS bedrock values taken from Wheeler et al. (1999) are in *italics*. **Bottom Panel:** Theoretical speleothem compositions based on dissolution of bedrock plus additional Mg and Sr from modern-day seasalt input. $D_{Mg} = 0.031$, and $D_{Sr} = 0.083$.

Pure Dissolved Bedrock	Dripwater						Speleothem		
	[Ca]	[Mg]	[Sr]	[Na]	Mg/Ca	Sr/Ca	Sr/Ca	Mg/Ca	Sr/Mg
	Mol %	Mol %	ppm	ppm	mmol mol ⁻¹	mmol mol ⁻¹	mmol mol ⁻¹	mmol mol ⁻¹	mol mol ⁻¹
High-Mg Calcite	91.7	8.3	3.5	105	91	4.0	0.3	2.8	0.119
CM Dolomite	<i>58.6</i>	<i>41.4</i>	<i>234</i>	<i>386</i>	<i>706</i>	<i>267.3</i>	22.2	21.9	1.013
CS Dolomite	<i>55.1</i>	<i>44.9</i>	<i>142</i>	<i>241</i>	<i>815</i>	<i>162.2</i>	13.5	25.3	0.533
CMS Dolomite	<i>57.8</i>	<i>42.2</i>	<i>214</i>	<i>330</i>	<i>730</i>	<i>244.4</i>	20.3	22.6	0.896

Bedrock Plus Current Seasalt	Dripwater						Speleothem		
	[Ca]	[Mg]	[Sr]	[Na]	Mg/Ca	Sr/Ca	Sr/Ca	Mg/Ca	Sr/Mg
	Mol %	Mol %	ppm	ppm	mmol mol ⁻¹	mmol mol ⁻¹	mmol mol ⁻¹	mmol mol ⁻¹	mol mol ⁻¹
High-Mg Calcite					474	3.9	0.3	14.7	0.022
CM Dolomite					1090	267.1	22.2	33.8	0.656
CS Dolomite					1199	162.1	13.5	37.2	0.362
CMS Dolomite					1114	244.3	20.3	34.5	0.587

Figures

Fig. 1. Gradient maps of Pacific rainfall during Southern Hemisphere Winter (**Top Left**) and Southern Hemisphere Summer (**Top Right**) with the location of Niue Island (red cross). **Bottom Panel:** Map of Niue with the location of the cave marked by crosshairs (left) along with a plan view of the study cave (right).

Fig. 2. **Left:** Automated dripwater collection carousel. **Right:** Dripwater collection bottle with floating ball that seals the bottle to prevent evaporation and CO₂ degasing.

Fig. 3. Niue cave dripwater δD versus $\delta^{18}O$. Open symbols represent weekly-integrated samples collected with the automated carousel sampler. A best-fit line through all data is described by the equation $\delta D = 7.8 \times \delta^{18}O + 9.6$, which is nearly indistinguishable from the Global Meteoric Water Line (GMWL; Craig 1961; Dansgaard, 1964) and the South Pacific Meteoric Water Line (SPMWL; Aharon et al., 2006). The highlighted box illustrates that dripwaters with $\delta D \geq -26$ ‰ were exclusive to dry winter periods. Rainfall weighted mean calculated from GNIP Rarotonga Station 9184300 from 1979-1991.

Fig. 4. **Panel A:** Cumulative weekly precipitation (red; P), calculated apparent evapotranspiration (gray; ET), and calculated net rainfall (blue; P-ET). Orange and blue bars at top indicate austral summer (wet) and winter (dry). **Panel B:** Niue cave dripwater δD (red) and $\delta^{18}O$ (blue) timeseries plotted with 1-sigma analytical error bars. Horizontal dashed blue line indicates dripwater isotopic averages ($\delta D = -27.1\text{‰}$; $\delta^{18}O = -4.7\text{‰}$). Horizontal dotted black line indicates volume weighted mean isotopic composition of Raratonga rainfall (GNIP Station #9184300 from 1979-1991). **Panel C:** Niue cave dripwater chloride (red) and sodium (blue) concentrations. **Panel D:** Dripwater Mg (red) and SO_4 (blue) concentrations. **Panel E:** Dripwater Ca (red) and Sr (blue) concentrations. Ionic concentrations were elevated through November 2012. After the onset of late-summer rainfall, concentrations began to trend downward. [Na] and [Cl] decreased by 18%, while [Mg], [Ca], and [Sr] decreased by 7, 9 and 4% respectively. Gaps in data are a result of equipment malfunction.

Fig. 5. Niue dripwater element to chloride ratios plotted with lines indicating seawater (SW) ratios. Red lines are linear best fit for all data. All dripwaters plot above their respective SW ratio, indicating that SW contributes a significant amount of each element *in addition to* contributions from dissolved bedrock and evolution via PCP.

Fig. 6. Niue dripwater X/Ca versus Mg/Ca ratios. Solid lines in first five panels are linear best-fit lines through all data. Also shown is the modeled PCP vector for Sr/Ca vs. Mg/Ca, where starting dripwater composition is: $[\text{Ca}^{2+}] = 5,000 \text{ } \mu\text{mol L}^{-1}$, $[\text{Mg/Ca}] = 100 \text{ mmol mol}^{-1}$, and $[\text{Sr/Ca}] = 1.8 \text{ mmol mol}^{-1}$.

Fig. 7. **Panels A-E:** Niue cave dripwater element to calcium (X/Ca) and Sr/Mg ratio timeseries. Dripwater X/Ca ratios covary throughout the study period, suggesting that PCP is the primary driver of hydrochemical evolution. Dripwater Sr/Mg ratios slowly increased after January 2013, when increased rainfall resulted in dilution of seasalt-derived ions (see Fig. 3 for concentration timeseries). Since a larger fraction of Mg is seasalt-derived, Sr/Mg ratios trended upward. A Stineman function (geometric weight to current point $\pm 10\%$ of data range; Stineman, 1980) is applied to Sr/Mg ratios for a local smoothing effect. **Panel F:** Cave air partial pressure of CO₂ (blue). The solid gold line indicates atmospheric pCO₂, concurrently ~ 395 ppmv. The data gap in 2013 resulted from instrument failure. **Panel G:** Niue cave dripwater data indicate loss of solution from overflow reservoirs due to torn collection bags and are therefore minimum estimates of actual drip rate. The red dashed line in 2012 indicates that dripwater bottles were full and were not outfitted with overflow bags, therefore these data are minimum estimates. Gaps in the data (J-O, 2013) are due to equipment malfunction.