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Article

Abiotic and Biotic Processes Controlling Deposition of Calcite and Hydrotalcite Calcretes on Niue Island, Southwest Pacific

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Abstract: Calcretes are indurated terrestrial carbonates that are widespread in arid and semi-arid settings and serve as important archives of present and past environments. Here we use geochemical tools to explore the nature and origin of calcretes documented from tropical Niue Island in the Southwest Pacific. The study recognizes two types of calcretes that differ in their mineral assemblage, microfabrics, elemental chemistry and carbon and oxygen isotopes. The calcretes common in the paleo-lagoon soils consist of 90% low-Mg calcite and ~10% highly weathered Mg-Al silicates. These pedogenic calcretes formed in the soil profiles within the vadose zone and bear the following distinctions: (i) Fe/Al ratio of 0.75, identical to the ratio in soils (Fe/Al=0.76 ±0.5), substantiates the link between the calcretes and soils; (ii) presence of rhizoliths, root voids, micritic nodules and clasts are consistent with a pedogenic calcrete fabric, and (iii) ¹³C and ¹⁸O depletions of -10.6‰ and -5.3‰, respectively, are compatible with carbon sources from microbial and roots respiration, and formation in oxygen isotope equilibrium with vadose waters. Unlike the pedogenic calcrete, a rare calcrete from the coastal terrace contains an exceptionally rare hydrotalcite mineral (65%) coated by microbial films. We contend that the hydrotalcite-rich calcrete was deposited through interaction of dolomite with seawater, similar to the method of producing hydrotalcite in the laboratory. ¹³C and ¹⁸O enrichments of 0.8 to 1.7‰ and -1.0 to -1.6‰, respectively, are in agreement with (i) mixed carbon sources consisting of microbial CO₂ degassing, seawater HCO₃ and dolomite dissolution, and (ii) oxygen isotope equilibration with a seawater-derived fluid.

Keywords: calcrete; biotic and abiotic processes; geochemical assays; origin; provenance; archives of environment and ecology

1. Introduction

Two types of carbonate-rich calcretes have been documented from Niue Island in the Southwest Pacific (Figure 1). One is commonly associated with the island interior soils (Figure 2 A) (Whitehead and Aharon, 2023). The other, confined to the coastal terrace, is uncommon and has been described from field observations as a “Palagonite tuff” by Marsden (1964) and Schofield (1967), and an “Iron-rich deposit” by Nunn and Britton (2004) (Figure 2 B). Neither one of those studies substantiated the field observations with laboratory investigations.

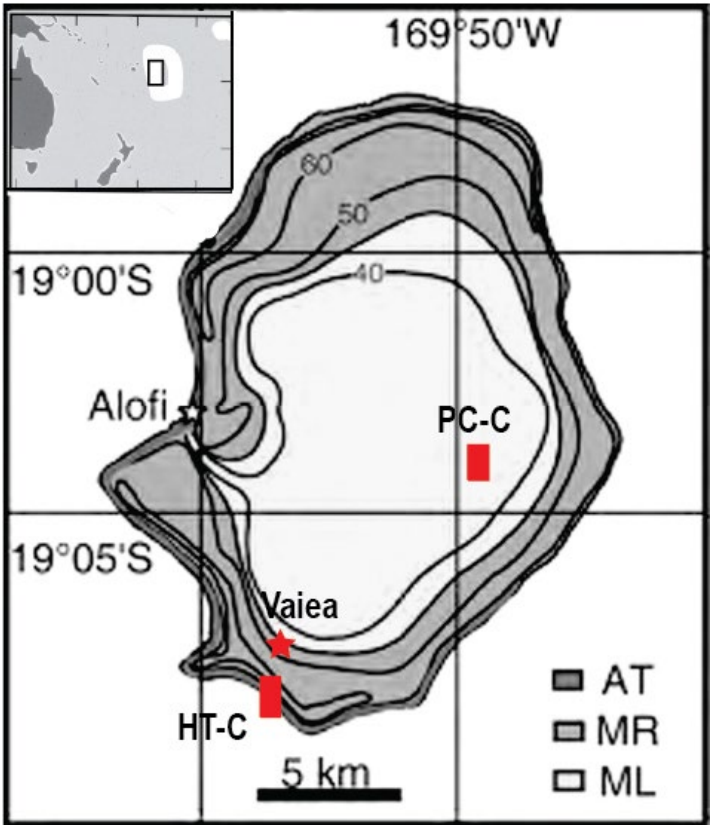


Figure 1. Location map of Niue Island in the Southwest Pacific (inset map), and location of the calcretes investigated in this study (PC-C=calcite-rich calcrete; HT-C=hydrotalcite-rich calcrete) related to the major geologic units identified in Niue. AT=Alofi Terrace; MR=Mutalau Reef; ML=Mutalau Lagoon (see text).

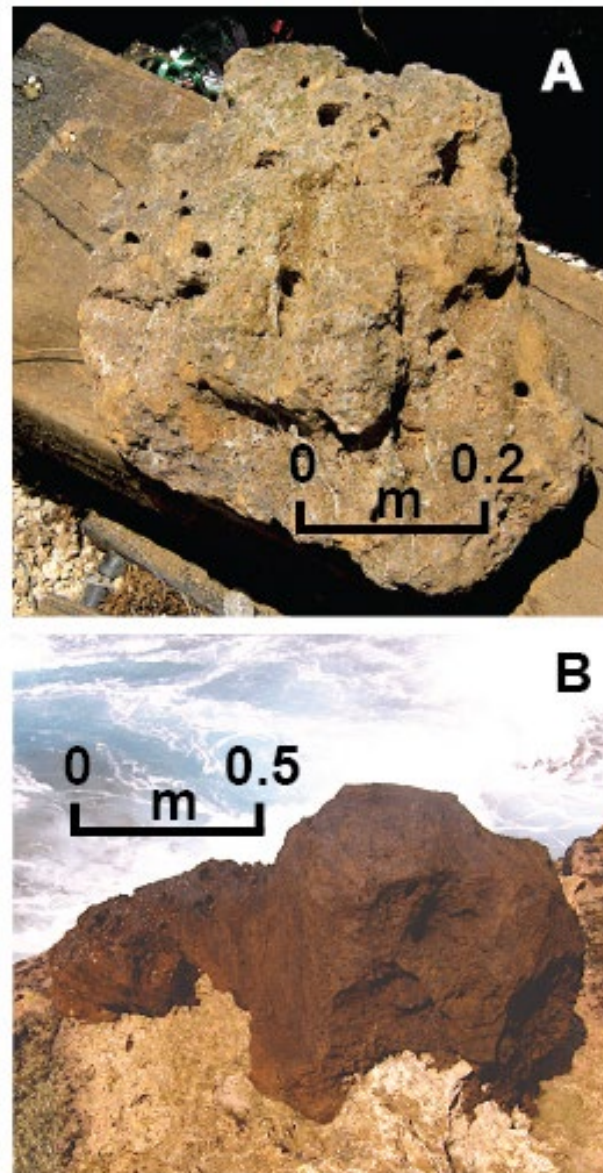


Figure 2. Field views of (A) PC-C underlying soil, and (B) subaerially exposed HT-C. Note the contrast in color and in the macroporosity between the two calcretes.

Here we report the results of a laboratory investigation of the two contrasting calcrete types occurring in Niue Island. The calcrete block exteriors conceal their content (Figs. 2 A and 2 B) and therefore examination in the field offers no clues as to their origin and provenance. In this study we employ X-Ray Diffraction (XRD) to identify the calcrete mineral constituents, and petrographic microscopy of thin sections to unravel the microfabrics of the minerals and organic residues. Additionally, we acquired elemental chemistry and stable carbon and oxygen isotopes from hand-size subsamples to discern origin and provenance. In conjunction, the results afforded deduction of the factors controlling deposition in a sedimentary setting atypical of calcrete formation (Milnes, 1992; Alonso-Zarza and Wright, 2010).

2. Niue Island Setting

Niue Island is an uplifted former atoll in the tropical Southwest Pacific and, at 259 km², one of the largest carbonate islands in the region (Figure 1). The geology and landscape of the island have been shaped primarily by (i) early subsidence of the underlying extinct volcano during Early-Mid

Miocene to Pliocene (Schofield, 1959; Hill, 1983; Lu et al., 1996); (ii) uplift since early Pleistocene resulting from upwarping of the lithospheric plate as it travels toward the Tonga Trench (Dubois et al., 1975); (iii) sea-level fluctuations since Late-Miocene time (Aharon et al., 1993; Wheeler and Aharon, 1997), and (iv) enhanced sediment transport and erosion associated with the sea-level cycles and frequent cyclones (Kennedy et al., 2012; Marsters and Kennedy, 2014). The depositional history of the carbonate sediments in Niue, comprising limestone, dolomite and remnant coral aragonite, has been investigated in outcrops, quarries (Schofield, 1959; Paulay and Spencer, 1992; Nunn and Britton, 2004; Kennedy et al., 2012; Marsters and Kennedy, 2014) and cores up to 320 m long (Aharon et al., 1993; Lu et al., 1996; Wheeler et al., 1999).

The island geology is differentiated into a modern to mid-Holocene age shore platform at sea-level (Kennedy et al., 2012), a prominent Alofi Terrace of Late Pleistocene-age rising to an elevation of about 20-23 m asl, and a Late Miocene to Pliocene-age Mutalau Atoll, consisting of a lagoon enclosed by a ridge that preserve the former coral atoll topography (Schofield, 1959).

Niue is blanketed by a thin veneer of ~35 cm thick, highly weathered, soils dominated by Fe and Al minerals consisting of goethite, gibbsite and boehmite (Whitehead and Aharon, 2023). The soils have been systematically sampled and investigated in order to explain the origin of their unusually high radioactivity (Fieldes et al., 1960; Schofield, 1967; Whitehead et al., 1993, among others). The Alofi Terrace and the seaward slopes are mantled by tropical black earths (Wright and Van-Westerndorp, 1965). The soils on the remainder of the island are tropical terra rossa that are low in silica and high in iron oxide and alumina. Lithified red to light-brown colored terra rossa soil filling sinkholes in the carbonate sands and overlying massive dolomite is commonly observed in the former lagoon (Figure 3). The provenance of the highly weathered Niuean soils has long been a subject of debate, bearing on three explicit sources: (i) volcanic ash and meteoric dust (Fields et al., 1960); limestone from the carbonate platform (Whitehead et al., 1993), and (iii) pumice rafts (Whitehead and Aharon, 2023).

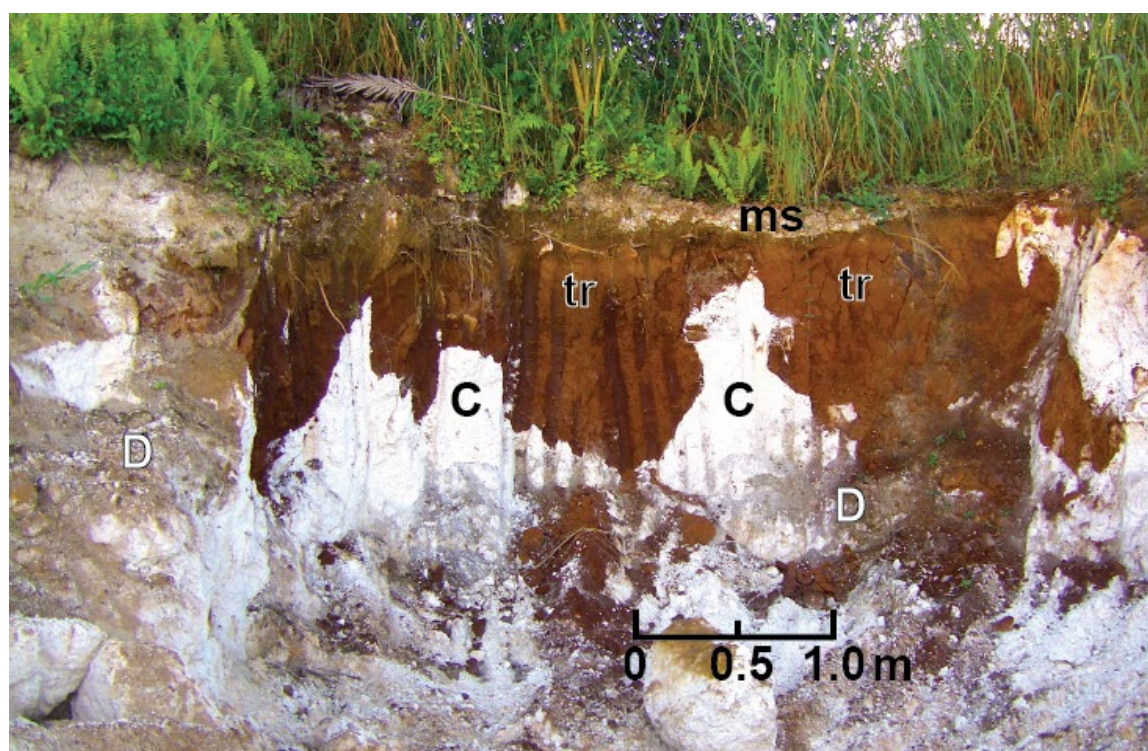


Figure 3. Light brown to red-colored terra rossa soil (tr) filling sinkholes in carbonate sands (C) of the Mutalau Lagoon, and underlying a thin layer of modern soil (ms). The white, chalky carbonate-sand overlies massive dolomite (D).

Occurrence of odd, solitary rocks underlying soils and overlying sediments on Niue have long been known to the locals who nicknamed the more common yellowish-gray as “Brown Rock” (Figure 2 A) and the scanty reddish-brown as “Black Rock” (Figure 2 B). Marsden (1964) described a solitary “Black Rock” found on a shelf ~ 3m asl on the northwest side of Niue as an “oxidized, yellow palagonite-cemented tuff with a hard, thick dark-brown crust containing much CaCO_3 and appearing slightly permeable” (Marsden, 1964, p. 818-819). Neither the collected sample, or the field location have been ever found (Schofield, 1967). More recent, Nunn and Britton (2004) reported of another “Black Rock” type the authors examined on the southern coast near Vaiea (Figure 1). This “Black Rock”, about 1.1 m in length, projects from the edge of the terrace at ~3.2 m asl and is frequently engulfed by the waves (Fig 2 B). These authors (op.cit.) identified the rock as an “iron-rich deposit” formed by groundwater in cracks within the limestone platform. Survival of the rock in a high-energy environment was explained by its higher resistance to erosion than the surrounding limestone (Nunn and Britton, 2004). Unlike the scarcity of the “Black Rock”, the distribution of the rectangular-flat “Brown Rock” is geographically wider and commonly occurs underlying the soil blanketing the ancient Mutalau barrier reef (i.e., “makatea”) and lagoon (Whitehead and Aharon, 2023) (Figure 2 A).

A “Brown Rock” from the top of the lagoon interior and a “Black Rock” from the coast near Vaiea were investigated in the field and representative subsamples were taken for further studies. Field observations identified the rocks as “calcretes” (Whitehead and Aharon, 2023). In the following we report on the laboratory methods we employed and the analytical results rendering data on the mineral constituents, textural relation between components, elemental chemistry and carbon and oxygen isotopes that have a bearing on the origin and provenance of the calcretes.

3. Methods and Results

3.1. Mineral Compositions

Several grams of representative rock samples were powdered in an agate mortar, thoroughly mixed and bottled in sealed vials. The mineralogy of the randomly oriented powders was determined by X-Ray Diffraction (XRD) using a benchtop Bruker X-Ray Diffractometer. XRD data was collected with $\text{Cu K}\alpha$ radiation by step-scans at $0.04^\circ/2\theta$ increments with fixed counting time of 1.0 sec. Automated quantitative calibration of mineral weight percentages was based on integrated peak intensity procedures.

The XRD scans, shown in Figures 4 A and 4 B, exhibit major dissimilarities between the calcretes. The mineralogy of the “brown rock” (henceforth, PC-C) presents no surprises. It is dominated by low- magnesium calcite at ~90% abundance, followed by a small but significant assemblage of Mg-Al silicates (goethite and gibbsite) and a hydrated Ca-Al phosphate $[\text{CaAl}_3(\text{PO}_4)(\text{PO}_3\text{OH})(\text{OH})_6]$ amounting to ~10% abundance. The peaks of gibbsite and crandallite-related mineral carry a significant uncertainty arising from the overshadowing of the dominant calcite peaks. In contrast, the dominant carbonate minerals in the “Black Rock” (henceforth, HT-C) are hydrotalcite and magnesian-calcite at 65% and 30% abundance, respectively. Traces of goethite are present in the XRD scan (Figure 4 B). The carbonate minerals of powder aliquots from the two calcretes were preferentially dissolved with dilute HCl and filtered in order to examine the insoluble residue (IR). Concentration of the IRs by a magnet showed the presence of abundant magnetite clusters in the PC-C but total absence in the HT-C.

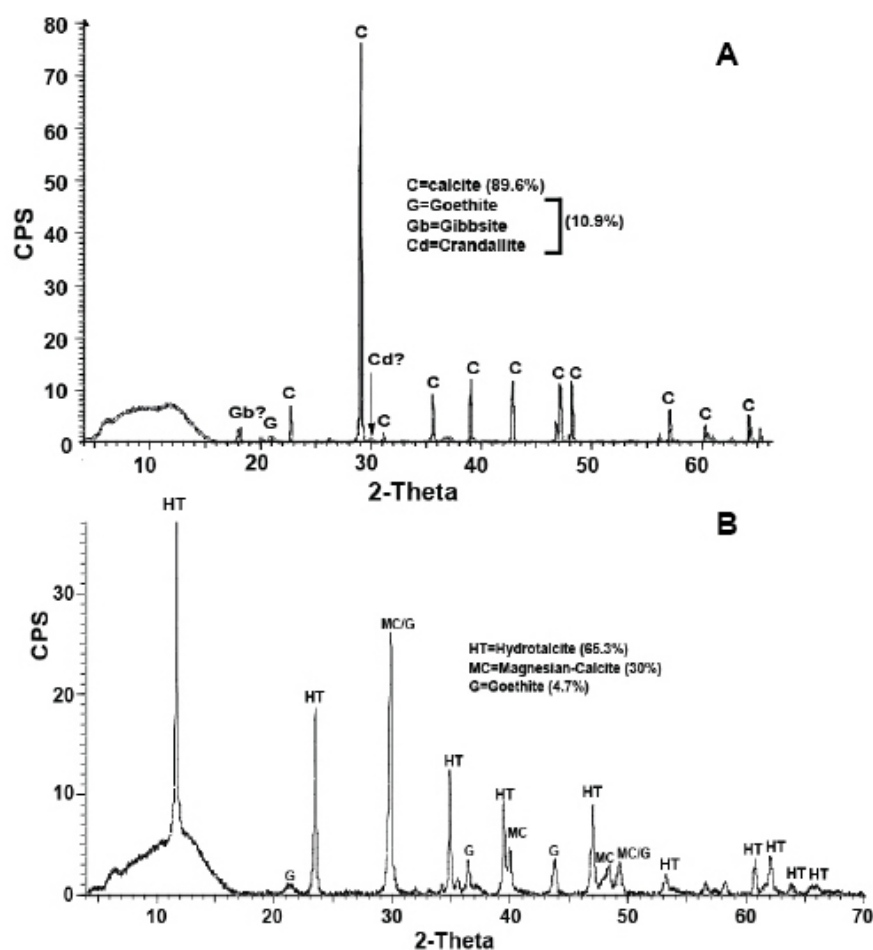


Figure 4. X-Ray powder diffraction pattern of (A) PC-C calcrete, and (B) HT-C calcrete. See text.

Hydrotalcite is a layered double Mg and Al hydroxy-carbonate hydrate (LDH) represented by the general formula $[Mg_6Al_2(CO_3)(OH)_{16}(H_2O)_4]$ (Forano et al., 2013). It is a rare natural mineral and is commonly found in association with weathered ultramafic and serpentinite rocks (O'Neil and Barnes, 1971; Stanimirova, 2001; Oskierski et al., 2013; Turvey et al., 2018). With the two exceptions below, hydrotalcite occurrences are exceptionally rare in sedimentary rocks. The exceptions are the occurrences of HT in high-Mg mudstones from the Kozani Basin in Greece (Hall and Stamatakis, 2000) and a sparse distribution in lithified terra rossa soils from Cayman Islands (Jones, 2021).

3.2. Microfabrics

Polished thin sections were prepared from the PC-C and HT-C and examined under a Nikon SMZ800 petrographic microscope using reflected light under a range of magnifications.

The most outstanding feature that clues in on the pedogenic origin of PC-C is the presence of organic matter-infilling voids and representing decayed root mats (Figure 5, A and B). The root voids have locally evolved into rhizoliths (calcified roots) as displayed in Figure 5 A, B and D. The presence of brown-micritic nodules, micrite screens around the root voids, mottled-gray calcites and calcite clasts (Figure 5 C) point to a pedogenic calcrete fabrics (Wright et al., 1988; Rasbury et al., 2000). Not unlike the PC-C, the HT-C also displays microfabrics typical of calcretes (Figure 5, A and B). In contrast to PC-C that exhibits high-porosity and immature rhizoliths, the HT-C is more compacted and shows lower porosity attributed to infilling of the rhizoliths with hydrotalcite coated by microbial films (Figure 5 A). Occasional dissolution voids are observed in Figure 5 B. The small snail shell that found shelter in the void is likely modern. The PC-C exhibits "immature" fabrics by

comparison with the HT-C's "mature" fabrics. On this basis we surmise that the former maybe of a younger age than the latter.

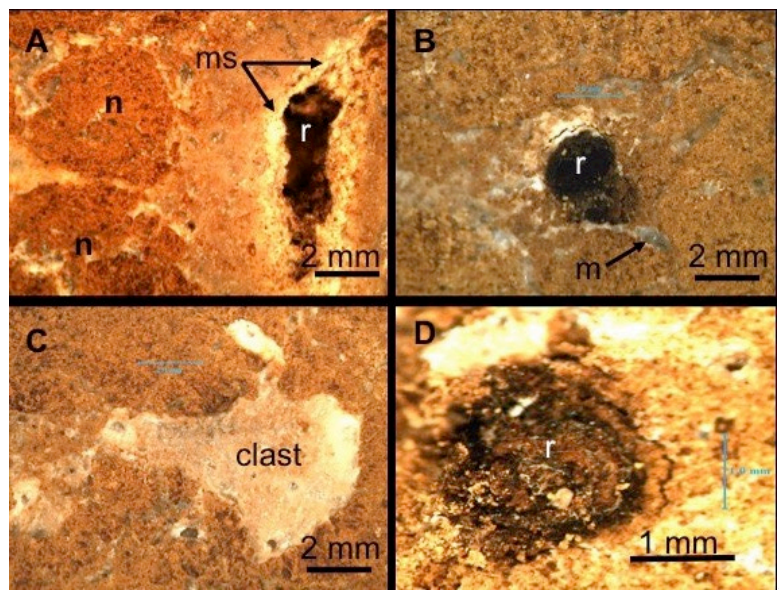


Figure 5. Photomicrographs in reflected light documenting the PC-C calcrite microfabrics. (A) n=calcite nodules; r=root molds (rhizoliths); ms=micrite screens formed around root voids. (B) m=mottled gray calcite. C=Large (>2mm) limestone clast. D=Large rhizolith filled by layered calcite.

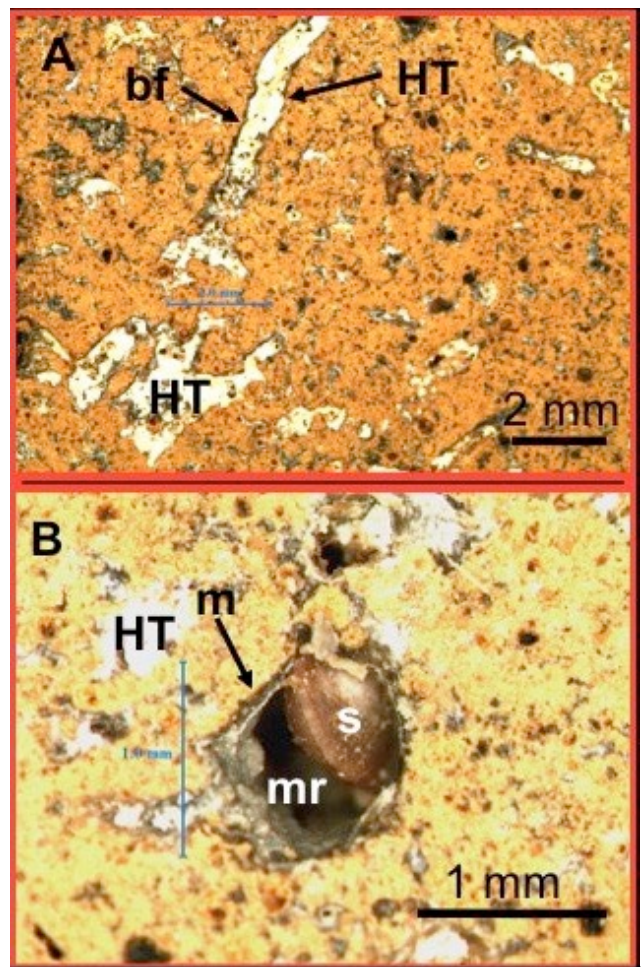


Figure 6. Photomicrographs in reflected light of hydrotalcite-rich calcrete (HT-C). A. HT=hydrotalcite-filled fractures encased in biofilms (bf). Note the absence of rounded nodules and lower porosity by comparison with PC-C calcrete. B. mr= fossil mold; m=gray mottle; s=small snail test that found shelter in the void.

3.3. Elemental Chemistry

Major oxides composition of PC-C and HT-C were determined by XRF on powdered samples prepared as fused disks, and the results are listed in Table 1. Table 1 also lists

Table 1. Elemental chemistry of selected elements in weight % in calcretes. Niue soils (A-horizon) data are from Whitehead et al. (1993) and list mean and SD values; n=number of analyzed soil samples.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	MgO/Al ₂ O ₃	Fe ₂ O ₃ /Al ₂ O ₃
PC-C	1.5	12.3	9.3	0.6	36.5	0.05	0.75
HT-C	0.4	10.9	8.0	17.9	21.1	1.6	0.73
Niue Soils	0.82 ±0.6	23.5 ±10.8	17.9 ±8.6	0.9 ±2.0	10.4 ±11.8	0.04 ±0.1	0.76 ±0.5
n	(n=89)	(n=107)	(n=89)	(n=94)	(n=115)		

Silica is ~3.7 times higher in PC-C relative to HT-C whereas the latter has ~30 times more Mg than the former (Table 1). The discrepancies are attributed to higher abundance of detrital silica-rich minerals inherited from the soils in PC-C, and the Mg enrichment in HT-C is explained by the dominant presence of Mg-rich hydrotalcite and magnesian calcite.

A Weathering Index (WI) developed by Whitehead and Aharon (2023) serves as a useful indicator of the preferential silica removal during weathering relative to the sum of iron and aluminum concentration: (SiO₂/(Al₂O₃+Fe₂O₃)). Both calcrete types exhibit exceptionally low WIs values of 0.069 and 0.021 suggesting a high degree of weathering that compares well with the mean WI of 0.02 of the highly weathered Niue soils (Table 1).

3.4. Carbon and Oxygen Isotopes

Well mixed powdered aliquots of ~1.0 mg by weight of PC-C and HT-C were reacted with 100% orthophosphoric acid at 50°C. The carbon and oxygen isotope values of the evolved and purified CO₂ were determined in a continuous flow mode (CF) using a Gasbench coupled to a modified Delta-Plus Isotope Ratio Mass Spectrometer (CF-IRMS). The ¹³C/¹²C and ¹⁸O/¹⁶O ratios are reported in the conventional delta (δ) notation in per mil (‰) relative to the Vienna-Pee Dee Belemnite (V-PDB). Analytical precision for both oxygen and carbon based on standard and sample repeats is ±0.1‰ (1σ). Water δ¹⁸O values listed below are reported on the conventional V-SMOW scale. Conversion from the V-PDB to V-SMOW scale is given by the equation (Kim et al., 2015):

δ¹⁸O (V-PDB)=0.97001* δ¹⁸O (V-SMOW)-29.99

(1)

Because the NBS-19 standard is a calcite, no kinetic fractionation factor correction associated with the acid reaction to liberate CO₂ was necessary for δ¹⁸O of calcite-dominated PC-C samples. In contrast, the kinetic fractionation factor correction for hydrocalcite-dominated HT-C samples is unknown and hence no correction to the δ¹⁸O values was performed. The total range of the correction factor for a wide range of carbonates is only 1‰ and therefore ignoring it should introduce only a

small uncertainty in $\delta^{18}\text{O}$ values of hydrocalcite, not exceeding several tenths of a permil (O’Neil and Barnes, 1971).

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ composition of the paired calcrete subsamples are listed in Table 2. Significant isotope differences observed between the PC-C and HT-C can be summarized as follows. PC-C exhibits substantially greater ^{13}C and ^{18}O depletions (-10.5 to -10.7‰ V-PDB and -5.2 to -5.4‰ V-PDB, respectively) relative to the HT-C (0.8 to 1.7‰ and -1.0 to -1.6‰ V-PDB, respectively).

Table 2. Carbon and oxygen isotopes of paired subsamples from the calcite-rich (PC-C) and hydrocalcite-rich (HT-C) calcretes in Niue Island. Note the contrasting isotope compositions between the two calcrete types.

Sample	$\delta^{13}\text{C}$ (‰ V-PDB)	$\delta^{18}\text{O}$ (‰ V-PDB)	$\delta^{18}\text{O}$ (‰ V-SMOW)
PC-C (1)	-10.7	-5.4	25.4
PC-C (2)	-10.5	-5.2	25.6
HT-C (1)	0.8	-1.6	29.3
HT-C (2)	1.7	-1.0	29.9

The ambient conditions conducive to the deposition of PC-C can be established on the basis of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values because equilibrium isotope fractionations between calcite and Dissolved Inorganic Carbon (DIC) and calcite- H_2O are well known (Salomons and Mook, 1986; Kim and O’Neil, 1997). We contend that the PC-C calcrete was formed in isotope equilibrium with the soil fluids on the basis of the following considerations. Measured $\delta^{13}\text{C}$ of DIC from Niue are $-11.7 \pm 2.3\text{‰ V-PDB}$ (n=6) in drips from caves representing water in the vadose zone, and $-9.1 \pm 2.7\text{‰ V-PDB}$ (n=18) in groundwater (Aharon et al., 2006). Assuming an ambient soil temperature of 25°C which is the annual average air temperature at Niue, the predicted $\delta^{13}\text{C}$ composition of a calcite in isotope equilibrium with the DIC would be -8.2 to -10.8‰V-PDB that are, given the uncertainties, in good agreement with the measured $\delta^{13}\text{C}$ values in PC-C (Table 2). On the basis of a radiocarbon material mass balance, Aharon et al. (2006) estimated that up to 91% of the carbon in the vadose zone is derived from soil CO_2 microbial respiration ($\delta^{13}\text{C}=-29.4\text{‰ V-PDB}$) and the remainder of 9% from dissolution of the underlying limestone/dolomite ($\delta^{13}\text{C}=-0.4 \pm 0.9\text{‰ V-PDB}$, n=149).

Drips from tips of stalactites in coastal caves and groundwater wells on Niue yield $\delta^{18}\text{O}$ compositions of $-4.5 \pm 0.1\text{‰ V-SMOW}$ (n=5) and $-4.5 \pm 0.14\text{‰ V-SMOW}$ (n=18), respectively, that represent the mean values of annual rainfall (Aharon et al., 2006). Using the temperature-depended $\text{CaCO}_3\text{-H}_2\text{O}$ experimental equation of Kim and O’Neil (1997), a predicted calcite deposited in isotope equilibrium with the Niuean waters at the ambient annual temperature of 25°C would yield a $\delta^{18}\text{O}$ of -7.1‰V-PDB. The predicted value is roughly close to the measured $\delta^{18}\text{O}$ values of the paired PC-C samples (Table 2) considering the likely effect of slight evaporation of the soil fluids that will cause ^{18}O -enrichment in the water, and the uncertainty of soil temperature.

Reconstruction of the ambient conditions conducive to hydrotalcite deposition from carbon and oxygen isotopes is complicated. That is because, with the singular exception below, no studies have reported stable C and O isotope data for pure hydrotalcite, or samples containing hydrotalcite in sedimentary rocks. Exceptional are the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ reports of one hydrotalcite associated with serpentinite (O’Neil and Barnes, 1971) and hydrotalcite mineralization of ultramafic mine tailings (Oskierski et al., 2013; Turvey et al., 2018). Importantly, the isotope fractionations, either equilibrium

or kinetic, during hydrotalcite uptake of labile carbonate ions, structural OH groups and interlayer H₂O molecules are unknown. However, given the exposure of the HT-C to atmosphere and seawater (Figure 2 B) and the association with the Niuean dolomite as a principal source of Mg, we conjecture that the ¹³C and ¹⁸O enrichments in the hydrotalcite (Table 2) were controlled by mixing of three-sources (i) atmospheric CO₂ ($\delta^{13}\text{C} = -8.5 \pm 1\text{‰}$, Mavromatis et al., 2015); (ii) HCO₃ source in dolomite dissolution

($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of 1.2 to 2.8‰ and 2.8 to 4.2‰, respectively) (Wheeler et al., 1999), and (iii) structural OH and interlayer H₂O of seawater provenance (seawater $\delta^{18}\text{O} = -0.15\text{‰}$ V-SMOW, Aharon et al., 2006).

4. Discussion

Pedogenic calcretes composed of low-Mg calcite are terrestrial deposits of widespread occurrence that form in soil profiles within the vadose zone (Milnes, 1992; Alonzo-Zarza and Wright, 2010). Calcrete-bearing soils are most common in arid and semi-arid continental settings where annual rainfall amount is <760 mm and where evaporation exceeds rainfall (e.g., in Mediterranean climate) causing moist deficits (Alonzo-Zarza and Wright, 2010). Niue Island, located in the tropics, receives an annual rainfall of 2036 ± 538 mm (mean and SD over a 92 yrs period, Rasbury and Aharon, 2006), and as such it seems to be an atypical setting for calcrete formation. In the following we discuss the abiotic and biotic factors involved in the formation of the two contrasting PC-C and HT-C calcretes documented in this study.

4.1. The Rainfall Factor

Rainfall on Niue Island is highly variable on inter-seasonal and inter-annual time scales (Rasbury and Aharon, 2006; Aharon et al., 2006). The inter-seasonal variability is driven by the South Pacific Convergent Zone (SPCZ) that moves seasonally over Niue as an appendix of the Intertropical Convergence Zone (ITCZ). It results in a monsoon season from December to April with a mean monthly rainfall of 307 mm and an average monthly air temperature of 26°C, and a dry season from May to November with a mean monthly rainfall of 84 mm and a mean air temperature of 24°C. The El-Niño-Southern Oscillation (ENSO) phase changes with 4.3 to 6.0 years periodicity exerts a dominant role on rainfall variability on inter-annual intervals. Severe droughts are associated with El-Niño events, respectively (Aharon et al., 2006). The regularity of rainfall switches is interrupted periodically by powerful cyclones accompanied by torrential rainfall. Twelve tropical cyclones struck Niue in the time intervals 1970-1975 and 1980-1985 (Rasbury and Aharon, 2006). Importantly, there is no surface drainage on the island and consequently rapid rainfall infiltration occurs as a result of the high porosity of the carbonate sediments. It can be concluded, therefore, that large annual rainfall values are concealing the droughts on inter-seasonal and inter-annual time scales that are conducive to calcretes formation in Niue.

4.2. Abiotic and Biotic Factors

The data presented in the preceding section suggest that both abiotic and biotic processes are controlling the deposition of the PC-C calcretes. These are (i) excess evaporation over rainfall during droughts; (ii) dissolution of the carbonates and leaching of Ca in the vadose zone (iii) invasion of atmospheric CO₂; (iv) microbial and roots respiration in the soil rhizosphere controlling the pCO₂; (v) CO₂ degassing, and (vi) elevated Ca and HCO₃ solutes from biogenic and abiotic sources give rise to supersaturation and precipitation of low-Mg calcite.

The data acquired from the HT-C contradict previous identifications as a palagonite tuff (Marsden, 1964; Schofield, 1967) or iron-rich rock (Nunn and Britton, 2004) and establish pertinence to an exceptionally rare class of calcretes not previously acknowledged that are dominated by hydrotalcite. The hydrotalcite abundance in the HT-C calcrete rises questions on the source of Mg and the factors controlling its deposition. Association of hydrotalcite mineralization with serpentinite and ultramafic rocks and experimental studies prompted the suggestion that Mg released in the

groundwater by weathering and leaching of Mg-silicates (e.g., olivine) and /or Mg-hydroxides (e.g., brucite), react with atmospheric-derived CO₂ to produce layered double hydroxides (LDH) (Oskierski et al., 2013; Turvey et al. (2018; Scott et al., 2021). Absence of ultramafic rocks in the Niue shallow subsurface makes such a Mg-source unattainable. Here we propose that the Mg source is in the abundant dolomite underlying the Niuean soils (Figure 3).

On the basis of our observations and analytical data we propose the following model of HT-C calcrete formation: (i) erosion and transport of MgO-rich soil material from the nearest Mutalau crest to the terraced coast; (ii) dolomite dissolution and CO₂ uptake from atmospheric and seawater sources, and (iii) induration of the terra rossa soil with hydrotalcite and Mg-calcite. Our proposed HT-C depositional model is supported by the following arguments:

(i) Kennedy et al. (2012) study established that Niue Island has a high potential for sediment erosion and transport. The highly dynamic environment will account for the transport of terra rossa (Figure 3) to the coast (Figure 2 B).

(ii) Dolomite serves as the principal source of Mg.

(iii) The ¹⁸O-enrichment exhibited by the hydrotalcite+Mg-calcite minerals is consistent with deposition from seawater whose waves regularly flood the calcrete,

(iv) The ¹³C-enrichment is compatible with mixed carbon sources from microbial respiration, kinetic invasion of atmospheric CO₂, HCO₃ from seawater and CaMg(CO₃)₂ dissolution. Our proposed model of hydrotalcite precipitation by dolomite-seawater interaction is supported by Kameda et al. (2000) laboratory synthesis of hydrotalcite by reaction of dolomite with seawater.

5. Summary

(i) Droughts occurring on inter-seasonal and inter-annual frequencies frame the uplifted former atoll of Niue Island in the Southwest Pacific as a suitable setting for calcretes deposition.

(ii) Two types of calcretes have been documented on the island: (i) a “common” calcite-rich calcrete associated with the soils in the paleo-lagoon, and (ii) a unique hydrotalcite-rich calcrete occurring on the coastal terrace and bathed by high waves.

(iii) Biotic and abiotic factors promoting deposition of the calcretes were identified from application of geochemical assays of XRD, optical petrography, elemental chemistry and carbon and oxygen isotopes.

(iv) Evaporation of vadose groundwater, CO₂ derived from microbial and root respiration lowering the fluid pH and causing limestone dissolution, release of Ca in solution and calcite supersaturation are the primary factors controlling the pedogenic calcrete formation.

(v) Hydrotalcite minerals [Mg₆Al₂(CO₃)(OH)₁₆(H₂O)₄] are exceptionally rare in nature and therefore the occurrence of a hydrotalcite-rich calcrete is unique.

(vi) The plausible mechanism of hydrotalcite deposition is interaction between dolomite and seawater, a process analogous to the hydrotalcite synthesis in the laboratory.

(vii) Calcretes are important archives of the ambient terrestrial environments and ecosystems. A systematic sampling and laboratory studies of the calcretes in Niue Island offer valuable recorders of past rainfall variability and soil development changes in a understudied region of the Southwest Pacific impacted by droughts attributed to SPCZ and ENSO events.

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