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SHORT COMMUNICATION

Józef Kazmierczak · Stephan Kempe

Genuine modern analogues of Precambrian stromatolites from caldera lakes of Niuafo‘ou Island, Tonga

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Abstract Calcareous or dolomitic, often secondarily silicified, laminated microbial structures known as stromatolites are important keys to reconstruct the chemical and biotic evolution of the early ocean. Most authors assume that cyanobacteria-associated microbialitic structures described from Shark Bay, Western Australia, and Exuma Sound, Bahamas, represent modern marine analogues for Precambrian stromatolites. Although they resemble the Precambrian forms macroscopically, their microstructure and mineralogical composition differ from those characterizing their purported ancient counterparts. Most Precambrian stromatolites are composed of presumably in situ precipitated carbonates, while their assumed modern marine analogues are predominantly products of accretion of grains trapped and bound by microbial, predominantly cyanobacterial, benthic mats and biofilms and only occasionally by their physicochemical activity. It has therefore been suggested that the carbonate chemistry of early Precambrian seawater differed significantly from modern seawater, and that some present-day quasi-marine or non-marine environments supporting growth of calcareous microbialites reflect the hydrochemical conditions controlling the calcification potential of Precambrian microbes better than modern seawater. Here we report the discovery of a non-marine environment sustaining growth of calcareous cyanobacterial microbialites showing macroscopic and microscopic features resembling closely those described from many Precambrian stromatolites.

J. Kazmierczak (✉)
Institute of Paleobiology,
Polish Academy of Sciences,
Twarda 51/55,
00818 Warsaw, Poland
e-mail: jkaz@twarda.pan.pl
Tel.: +48-22-6978887
Fax: +48-22-6206225

S. Kempe
Institut für Angewandte Geowissenschaften,
Technische Universität Darmstadt,
Schnittspahnstr. 9,
64287 Darmstadt, Germany

Introduction

It has been proposed that early oceans on Earth and Mars had been sodium carbonate-dominated, highly alkaline solutions (Grotzinger and Kasting 1993; Kempe and Degens 1985; Kempe and Kazmierczak 1990, 1994, 1997). Recent studies indicate (Lowe and Tice 2004) that on Earth, nahcolite ($NaHCO_3$) was a primary evaporitic mineral of the marine 3.5–3.2 Ga sedimentary record. Galileo infrared spectra also suggest presence of sodium carbonate salts on the ice of Europa (McCord et al. 1999), indicating that its hypocryotic ocean may also be alkaline (Kempe and Kazmierczak 2002). Our hypothesis of an early alkaline ocean is based on research conducted in modern alkaline environments. The characteristic features of these environments are high concentrations of Na^+, K^+, CO_3^{2-}, PO_4^{3-}, SiO_2 and very low concentrations of Ca^{2+} and Mg^{2+}, high pH values and high carbonate mineral supersaturations. According to our model, the ocean was buffered throughout much of the Precambrian by high carbonate concentrations balanced by alkaline metal ions, allowing Ca^{2+} concentrations to rise only slowly. The rise in Ca^{2+} concentration near the end of the Precambrian in turn triggered, by way of biochemical Ca detoxification reactions, important bio-evolutionary changes such as the advent of biologically controlled (skeletogenic) calcification processes (Kazmierczak et al. 1985; Kempe and Kazmierczak 1994). New observations (Brennan et al. 2004; Petrychenko et al. 2005), based on analyses of major ion compositions of primary fluid inclusions from terminal Proterozoic and Early Cambrian marine halites, support such a scenario.

Characteristic features of many Precambrian marine sedimentary sequences are laminated macroscopic bodies known as stromatolites (e.g. Walter 1983). They are interpreted as products of benthic microbial mats composed predominantly by cyanobacteria (e.g. (e.g. Riding 2000). It is assumed that these mats either bound carbonate particles from the water column or precipitated carbonate minerals physiochemically (for review see e.g. Fairchild 1991; Ginsburg 1991; Grotzinger and Knoll 1999; Maslov 1961). It has even been suggested that most of the oldest (Archean) stromatolites could have originated from abiogenic carbonate precipitation from seawater (Grotzinger and Rothman 1996). Cyanobacteria are common in modern seas, but they fail to calcify and to produce calcareous structures. Modern marine stromatolites occurring in shallow hypersaline embayments like Shark Bay, Western Australia (e.g. Awramik and Riding 1988; Logan 1961; Playford and Cockbain 1976; Reid et al. 2003), along brackish coastline (e.g. Rasmussen et al. 1993) and marine intertidal/shallow subtidal settings like Grand Exuma Sound, Bahamas (Dill et al. 1986; Dravis 1983; Reid and Browne 1991; Reid et al. 2000; Riding et al. 1991), have often been discussed as potential analogues of Precambrian marine stromatolites. Their internal structure and mineral compositions show, however, principal differences from those observed in Precambrian forms (for review see e.g. Awramik and Riding 1988; Fairchild 1991; Ginsburg 1991; Riding et al. 1991).

To support the concept of an early alkaline ocean, it required showing that modern alkaline environments sustain in fact in situ carbonate precipitating cyanobacterial benthic communities producing stromatolite-like structures. Therefore, we studied a quasi-marine alkaline crater lake on Satonda Island, Indonesia (Kazmierczak et al. 2004; Kempe and Kazmierczak 1993), and we investigated the largest soda lake on Earth, Lake Van, Turkey (Kazmierczak et al. 2004; Kempe et al. 1991; López-Garcia et al. 2005). In both lakes, we have discovered in vivo calcifying cyanobacterial biofilms or calcareous structures produced by in situ calcifying cyanobacterial mats. These microbialites differ, however, significantly in internal structure and dimensions from Precambrian stromatolites. In an effort to find genuine analogues for Precambrian stromatolites and to define the conditions under which they form, we visited Niuafo‘ou, the northernmost island of the Kingdom of Tonga—also known as Tin-Can Island.

Materials and methods

The Niuafo‘ou stromatolites were investigated on macroscopic slabs and in petrographic thin sections under optical microscope. Scanning electron microscopy (SEM) at 25 kV was used for examining samples of air-dried mat surfaces sputtered with a 10- to 15-nm thick layer of platinum or carbon. SEM examinations and energy-dispersive spectroscopy (EDS) analyses have been performed using a Philips XL-20 scanning microscope equipped with EDS detector ECON 6, system EDX-DX4i and backscatter electron (BSE) detector for Compo or Topo detection (FEI product). X-ray diffraction (XRD) analyses of capillary carbonate micro-samples have been performed using a CGR-INEL diffractometer equipped with cobalt lamp and focusing goniometer with transmission optics for Debey–Scherrer powder preparations. Sampling of water samples was conducted by lowering a Niskin water bottle on a 6-mm rope by hand. $P\mathrm{CO_2}$ was determined preliminarily in the field with an infrared electrode; pH and alkalinity were also determined in the field. Atomic absorption spectrometry (AAS) for Ca and Mg was performed on water samples acidified with HNO_3. Anions were determined by ion chromatography. The calculation of saturation indices of main carbonate minerals and of $P\mathrm{CO_2}$ was done with the computer program PHREEQE (Parkhurst et al. 1980).

Results

Niuafo‘ou (175°37’W/15°36’S) is a circular volcanic island about 8 km in diameter, containing a 5-km wide caldera with steep inner walls rising 70 to 205 m above sea level (Fig. 1a). The caldera contains several lakes. The famous volcanologist T.A. Jaggar already noted in 1935 unspecified calcareous shore deposits there (Jaggar 1935), a hint we followed in organizing our expedition to the island in 1998.

We ran echo-sounding GPS-referenced profiles across Vai Lahi, the largest lake (13.6 km^2, 0.98 km^3, 121 m deep), and Vai Si‘i, the second largest lake (0.81 km^2, 0.012 km^3, 31 m deep), to generate the first bathymetric map of the lakes (Fig. 1). The composition of the lake waters (Table 1) shows that the two lakes are of low salinity (4.2–4.5 and 2.3–2.9 g/l, respectively) and differ in composition. Concentrations of all main cations and anions increase slightly with depth, and a chemocline separates a mixed, oxygenated layer at 42.5 m in Vai Lahi and at about 20 m in Vai Si‘i from an anaerobic, H_2S-containing bottom layer.

Chemically, the most important observation is the high alkalinity of the waters (15.7–18.6 and 6.3–10.9 meq/l in Vai Lahi and Si‘i, respectively). These are far higher than in modern seawater, making bicarbonate the second most concentrated anion after chloride (approximately 54 and 35 meq/l in the two lakes, respectively) and before sulphate (1.7 and 1.4 meq/l, respectively). Although the lakes are at sea level, their water is not derived from diluted seawater. This is best illustrated by comparing elemental ratios such as Na/Mg (2, 2.6 and 4.2 for Vai Lahi, Vai Si‘i and seawater, respectively) or Na/Cl (approximately 0.8 for both lakes vs 1.2 in seawater) between the lakes and seawater. Rather, the lakes represent autonomous hydrochemical systems, fed by rainwater and accumulating dissolved ions by reacting with volcanic rocks through silicate weathering. This weathering is powered largely by carbonic acid, explaining the high alkalinities. The lakes have high CO_2 pressure values at depth ($P\mathrm{CO_2}$, Table 1), which may in part arise from volcanic gas seeps, such as those observed at several sites along the southern lakeshore. In spite of

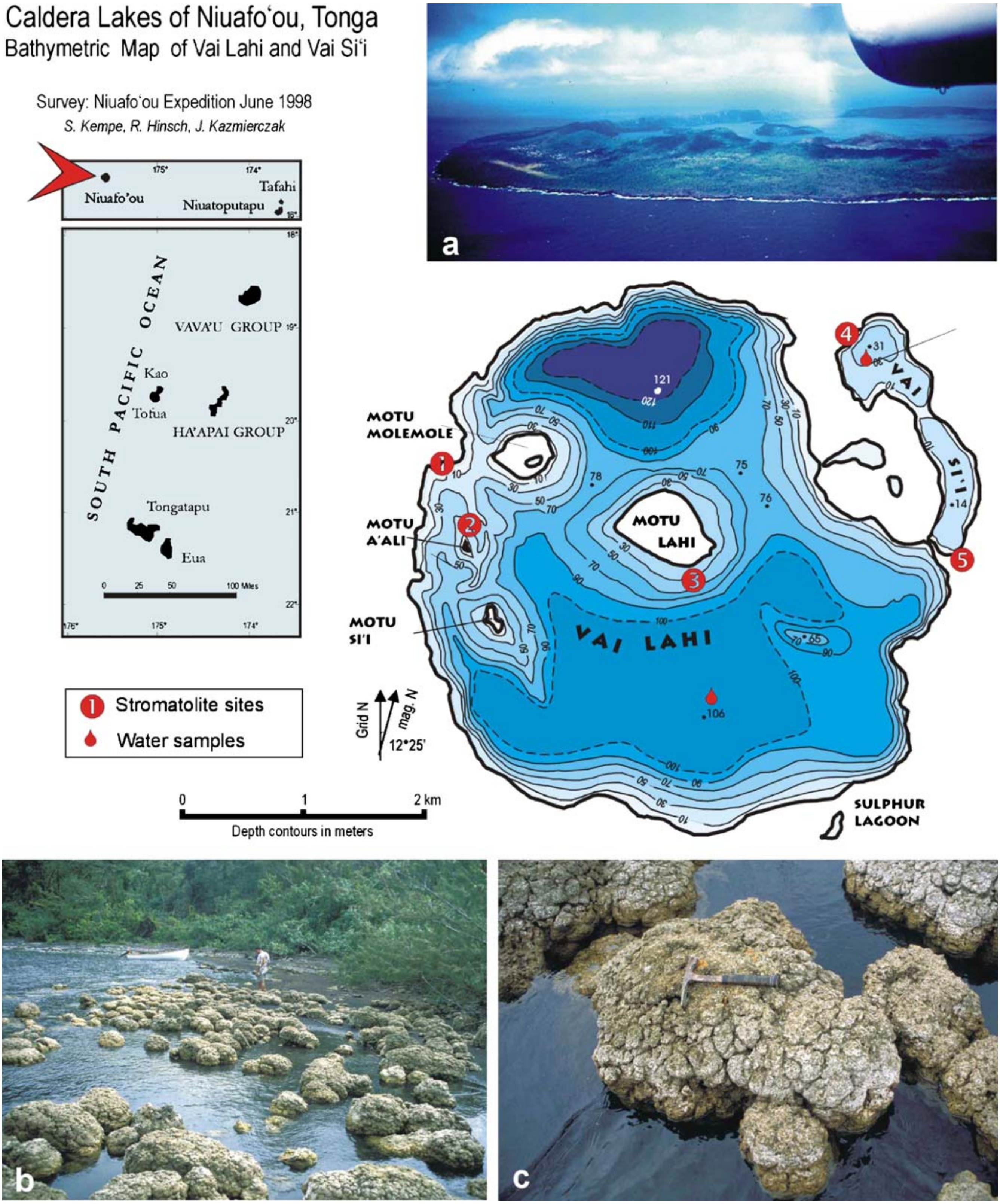

Fig. 1 Location of Niuafo'ou Island in Tonga Archipelago (*arrow head*). **a** Aerial view of caldera lakes of Niuafo'ou Island (photographed from northeast). Sites of stromatolite and water sampling are indicated on bathymetric map of the two largest lakes, Vai Lahi and Vai Si'i. **b** View of Vai Lahi stromatolite field. **c** An example of large Vai Lahi stromatolite (length of hammer, 28 cm)

Table 1 Chemical data of Niuafo‘ou lakes in 1998, compared to seawater

Sample	Depth (m)	pH	Alkalinity (meq/l)	Ca (meq/l)	Mg (meq/l)	SI_{Cc}	SI_{Ara}	SI_{Dol}	pCO_2 (ppmv)	$\delta^{13}C$ (PDB)
Vai Lahi										
W12	−10	8.35	15.7	0.71	21.04	0.65	0.50	2.94	3,180	
W3	−25	8.39	16.6	0.68	20.74	0.69	0.54	3.04	3,090	0.11
W9	−40	8.27	15.7	0.70	21.04	0.57	0.47	2.80	3,900	
W11	−42.5	8.13	16.6	0.78	20.85	0.52	0.37	2.63	5,810	
W10	−45	7.67	16.3	1.06	21.08	0.21	0.06	1.87	17,100	
W2	−50	7.73	18.8	1.12	21.10	0.34	0.20	2.12	17,100	−0.63
W1	−100	7.50	18.6	1.15	21.15	0.13	−0.02	1.68	29,200	−0.41
Vai Si‘i										
W15	−10	8.69	6.3	1.17	9.43	0.89	0.75	2.87	480	−1.98
W14	−30	7.25	10.9	2.32	11.99	0.04	−0.10	0.95	32,100	−2.67
Seawater	0	8.21	2.32	20.57	106.20	0.70	0.56	2.28	407	

Saturation index (SI)=[-log (ion activity product/$K_{mineral}$)]
Cc calcite, *Ara* aragonite, *Dol* dolomite

being wind-mixed, the epilimnion of Vai Lahi has a ten times higher PCO_2 than that of the atmosphere, suggesting a strong internal CO_2 source.

Several volcanic eruptions occurred during the last 100 years on the island, the last one was in 1946 (Rogers 1986). We measured the DIC-$\delta^{13}C$ value for some of the samples (Table 1) that show rather high values, again suggesting that the inorganic carbon does not derive from respiration of organic carbon. For instance, in Satonda crater lake, theses values range from −4.2 to −19.5, illustrating that the bicarbonate there is produced from organic carbon by way of sulphate reduction (Kempe and Kazmierczak 1993), a process dubbed as “alkalinity pump” (Kempe 1990; Kempe and Kazmierczak 1994). The high alkalinities in Vai Lahi cause a high supersaturation with regard to carbonate minerals; see Table 1 for saturation indices (SI). They are highest in the epilimnion of Vai Si‘i. Experience from other modern cyanobacterial microbialites sites (Kempe and Kazmierczak 1990, 1994; Merz-Preib and Riding 1999) shows that the SI of calcite or aragonite must be greater than approximately 0.8 before substantial precipitation of carbonates occurs. This is in accordance with the observations in Niuafo‘ou where we found vigorous calcification occurring in Vai Si‘i but weak or absent mineralization in Vai Lahi.

Along the shores of both lakes, we discovered head-like and crustose stromatolitic bodies either attached to lava blocks and steep rocky walls or to weakly cemented pumice sand. In Vai Lahi, large groups of head-like structures (Fig. 1b) displaying characteristic surface patterns reminiscent of tightly convoluted brains (Fig. 1c) have been encountered in three localities: in the shallow periphery of the western lake shore (Fig. 1, location 1) and on the shores of the islands of Motu A‘ali (Fig. 1, location 2) and Motu Lahi (Fig. 1, location 3). Some of the stromatolites protrude above the water table; some are subaerially exposed on the shore, up to 1–2 m above the present lake level, suggesting that they grew at higher lake level conditions. However,

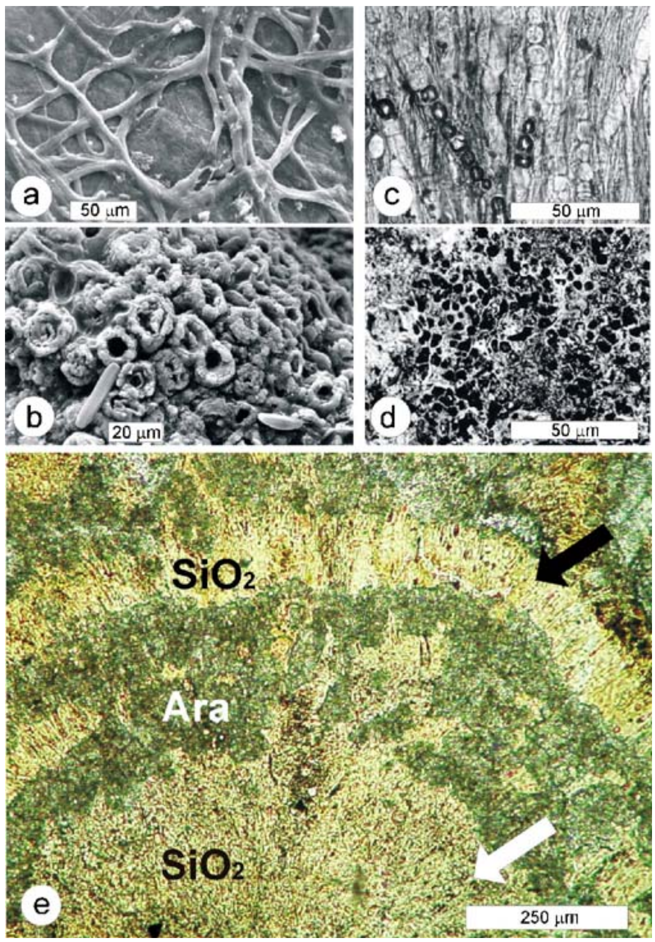

Fig. 2 SEM images of living filamentous (**a**) and coccoid (**b**) cyanobacteria from surface of Niuafo‘ou stromatolites from Vai Lahi (air-dried sample). **c**, **d** Optical vertical thin sections of silicified filamentous (**c**) and coccoid (**d**) cyanobacteria from fossilized parts of Niuafo‘ou (Vai Lahi) stromatolites. **e** Stromatolite layers composed of well-preserved silicified filamentous (*black arrow*) and coccoid (*white arrow*) cyanobacteria, alternating with obliterated cyanobacterial layers permineralized with aragonite (*Ara*)

most occur underwater and have been observed by free diving to a depth of several meters. The largest is over a meter in diameter, up to 80 cm tall, with a maximal thickness of the laminated calcareous body of approximately 30 cm. Closer examinations have revealed that the head-like stromatolites from Vai Lahi standing above the present-day water level are "dead" structures. Although their surfaces are often covered with a leathery layer of non-calcified filamentous (rivulariacean and/or oscillatoriacean) cyanobacteria (Fig. 2a) at the splash zone, they are clearly not in growth continuity with the previously formed calcareous stromatolite body. Surfaces of head-like stromatolites located permanently underwater are patchily covered by weakly in vivo calcifying capsular coccoid cyanobacteria (Fig. 2b). These and the filamentous forms are similar to remnants of calcified coccoid and filamentous microbiota preserved in places within the stromatolite bodies (Fig. 2c,d) and apparently participating in their origin (Fig. 2e). Numerous diatoms and ostracods are associated with the living cyanobacterial cover.

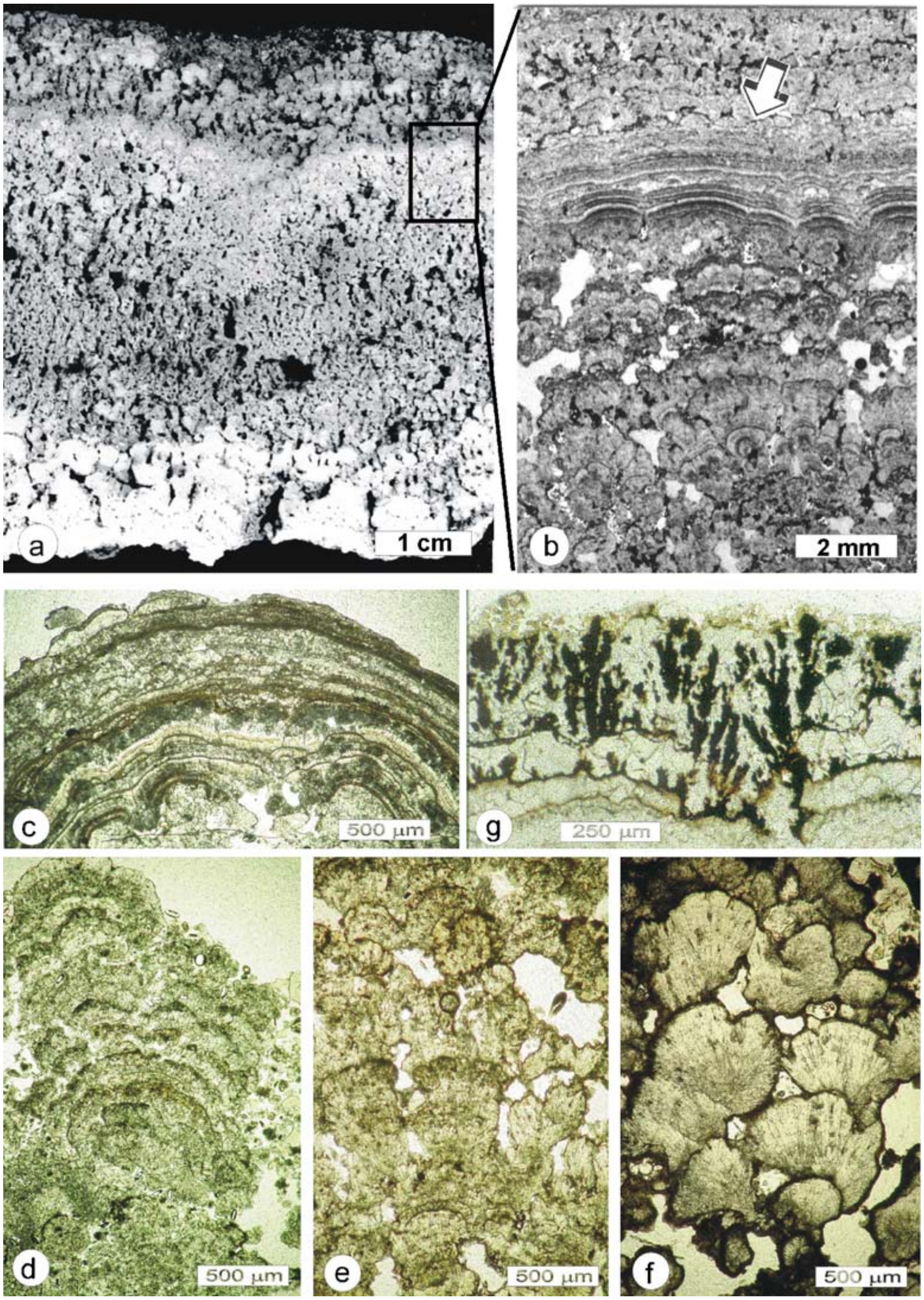

Fig. 3 **a**, **b** Vertical sections of polished slab of Vai Lahi stromatolite photographed at various magnifications to show the variety of its internal structure. **c**–**g** Optical micrographs showing selection of microstructures identified in vertical thin sections of Niuafo'ou stromatolites: **c** microlaminated, **d**, **e** microcolumnar (microstromatolitic), **f** cystous (tussock-like), **g** arborescent (*Frutexites*-like). *Arrow* in **b** indicates continuous transition from microlaminated to cystous microstructure

We dated the bases of three stromatolites and found uncalibrated ^{14}C ages of around 15,000 aBP. We also dated a piece of iron wood encased by cemented volcanic sand, yielding an uncalibrated ^{14}C age of 370±20 aBP. These dates suggest that stromatolites grew vigorously until quite recently in Vai Lahi. In Vai Si‘i, the SI_{Cc} is greater than 0.8 and SI_{Ara} is close to 0.8 (compare Table 1). Observations show that there are cyanobacterial mats that calcify intensively at present.

In vertical sections, the Niuafo‘ou stromatolites show an array of microstructures (micro-fabrics) closely resembling those described from Precambrian stromatolites (Buick et al. 1981; Fairchild 1991; Hofmann 1975; Knoll and Semikhatov 1998; Knoll et al. 1989; Semikhatov et al. 1979; Walter 1983). They are internally more or less distinctly laminated and composed of flat or undulating coarse- and fine-crystalline (micritic) aragonite layers varying in thickness (Fig. 3a,b). This differentiation correlates both with morphological characteristics of cyanobacterial taxa taking part in the formation of particular sets of laminae (Fig. 2e) and with the intensity of in vivo or early post-mortem biocalcification of the cyanobacterial biofilms. The biocalcification, in turn, is most probably reflecting the state of the carbonate system in the lake, particularly the level of calcium carbonate supersaturation, as shown for other modern in situ calcifying cyanobacterial microbialites (Kazmierczak et al. 2004; Kempe and Kazmierczak1990). In vertical thin sections, very fine laminated zones can be recognized (Fig. 3c), alternating often with microcolumnar (pillared) zones having microstromatolitic appearance (Fig. 3d) known from Proterozoic stromatolites (Pl. 8, Figs. 2 and 3 in Hofmann 1969; Fig. 4 in Buick et al. 1981; Fig. 2 in Hofmann and Jackson 1987; Figs. 4, 5 and 9 in Lanier 1988). In addition, tussock-like textures similar to those described from Proterozoic stromatolites (Fig. 2a in Bertrand-Sarfati 1976; Fig. 11a in Fairchild et al. 1990) are visible in cross-sections of some Niuafo‘ou stromatolites (Fig. 3e,f). Of particular interest are iron- and manganese-enriched calcareous micro-arborescent structures occurring in some subfossil stromatolites from Lake Vai Si‘i (Fig. 3g). They are comparable to fossil structures known as *Frutexites* (Fig. 10 in Horodyski 1975; Pl. 1, Figs. 10 and 11 in Walter and Awramik 1979; Figs. 7 and 9 in Myrow and Coniglio 1991). Almost identical structures occur in many Proterozoic and Palaeozoic carbonate microbialites, particularly in those growing near volcanic hydrothermal vents and supposedly linked to bacterial activity (see Walter and Awramik 1979 for review). Similarly as in many Precambrian stromatolites, the Niuafo‘ou calcareous microbialites are often early diagenetically silicified (Fig. 2e). As in some of their Precambrian analogues (e.g. Hofmann 1975), the silicified layers may enclose excellently preserved cyanobacteria sheaths (Fig. 2c,d).

Discussion

Our observations indicate that at present, the calcium carbonate supersaturation level in both of the studied Niuafo‘ou caldera lakes is not high enough to induce cyanobacteria to intensively precipitate and accrete calcium carbonate. This proves true particularly for Vai Lahi where SI_{Ara} is less than 0.8, and, therefore, the lake waters cannot sustain vigorous growth of the stromatolitic structures at present. We therefore must conclude that the massive large heads and crusts in Vai Lahi were formed not only at a higher lake level but also during conditions when the supersaturation was higher than at present.

Because textures and mineral composition of the Niuafo‘ou stromatolites are so similar to those of many Precambrian stromatolites, we conclude that the stromatolite-sustaining Precambrian seas generating carbonate cyanobacterial microbialites in their shallow areas were, similar to the Niuafo‘ou caldera lakes, alkaline carbonate systems (for other opinions on the early ocean chemistry see e.g. Bjerrum and Canfield 2002; Canfield 1998; Habicht et al. 2002; Holland 1984; Ohmoto 2004). Concerning the build-up of these conditions, Vai Lahi and Vai Si‘i represent therefore an interesting natural laboratory for modelling the chemistry of the Earth’s early hydrosphere which, according to current hypotheses, must have originated from the interaction of volcanic rocks, water and early atmospheric and volcanic gases (mainly CO_2). Finally, astrobiological aspects of our discovery cannot be overlooked. As shown by the current Spirit Rover mission to Gusev Crater on Mars, water-filled impact craters, similar to caldera lakes, may be the best sites to search for traces of past extraterrestrial life (Cabrol et al. 2001; Kempe and Kazmierczak 1997), particularly if they evolved alkaline conditions supporting growth of carbonate microbial structures like the Niuafo‘ou lakes.

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