

CONTRASTING STYLES OF CALCIFICATION BY THE MICRO-ALGA *OOCARDIUM STRATUM* NAEGELI 1849 (ZYGNETOPHYCEAE) IN TWO LIMESTONE-PRECIPITATING SPRING CREEKS OF THE ALPS

Diethard SANDERS¹⁾ & Eugen ROTT²⁾

KEYWORDS

¹⁾ Institute of Geology and Palaeontology, Faculty of Geo- and Atmospheric Sciences, University of Innsbruck, Innrain 52, 6020 Innsbruck, Austria.

²⁾ Institute of Botany, Faculty of Biology, University of Innsbruck, Sternwartestraße 15, 6020 Innsbruck, Austria.

[†] Corresponding author, diethard.g.sanders@uibk.ac.at

biocalcification
fibrous calcite
tufa limestone
microbialite
spring tufa
Oocardium

ABSTRACT

Because of their different chemical compositions, limestone-depositing cool springs provide natural laboratories that may unveil general lessons on carbonate deposition. An investigation of biocalcification of the unicellular desmid micro-alga *Oocardium stratum* in two spring creeks in the Eastern Alps revealed hitherto undescribed differences in calcification style. Distinct laminations of the deposit and seasonal variations of precipitation on artificial substrates suggest that calcification of *Oocardium stratum* takes places mainly spring and summer, although viable cells were found during the entire year. At location 1 (Lingenau), *Oocardium* limestone consists of 'seasonal' laminae 4–8 mm in thickness, produced by extensive biofilms composed almost entirely of *O. stratum*. Upon cell division and upward growth of *O. stratum*, tubes of rhombohedral calcite are formed which encase each unicell branch, too. During branching of tubes, the optical orientation of the calcite is retained. Upward growth of individual calcite tubes proceeds by stacking of ring-shaped laminae of calcite around each unicell of *O. stratum*. Numerous cell divisions and branching of calcite tubes result in 'bush-shaped' calcite biocrystals growing up to 10 mm in height per year. At location 2 (Alpenzoo), *O. stratum* calcifies in botryoids and laterally-merged botryoids of fascicular-fibrous calcite (ffC). On the botryoids, the cells tend to be more densely spaced than in the laminar biofilms of Lingenau. In thin section, *Oocardium* ffC can only be distinguished from abiotically-formed ffC by local presence of relictic structures left by growing *Oocardium* cells. At both locations, *O. stratum* seems to colonize pristine substrates exclusively on crystals of calcite that were, either, part of the substrate (e. g. limestone clasts) or induced by other biocalcifiers, or formed by abiotic precipitation from the spring stream. Comparison of both locations shows that 'Oocardium tufa', or 'Oocardium calcite', is not a single type of microfacies but is determined by the habitus of the abiotic cement at site. A preliminary comparison of abiotic calcite precipitation rates of an Alpine half-cave with *Oocardium* calcification suggests that the latter can be up to three orders of magnitude faster. Our observations suggest that cementstones in ancient reefs, and apparently abiotic seafloor precipitates of the geological past, may have formed in association with microbes.

Aufgrund der Unterschiede in der chemischen Zusammensetzung ihrer Wässer können kalkabscheidende kalte Quellen als natürliche Laboratorien angesehen werden, die möglicherweise verallgemeinerbare Aussagen zur Karbonatablagerung enthalten. Die Untersuchung der Biokalzifikation der einzelligen Mikro-Zieralge *Oocardium stratum* in zwei Quellbächen der Ostalpen zeigt bislang unbeschriebene Unterschiede in Art und Weise der Verkalkung auf. Die Ergebnisse der Fällungsprodukte an künstlichen Substraten zeigen eine stark bevorzugte Fällung im Frühjahr und Sommer, wenn auch an der Stelle Alpenzoo *Oocardium* mit ganzjährig grünen Zellen (allerdings in reduzierter Abundanz) beobachtet wurde. Die winterliche Verminderung der Kalkfällung könnte mit verstärktem Bewuchs durch Kieselalgen im Winter in Zusammenhang stehen. An Lokalität 1 (Lingenau) besteht der *Oocardium*-Kalk aus etwa 4–8 mm dicken Laminae pro Jahr, die von ausgedehnten Biofilmen aus nahezu ausschließlich *O. stratum* gebildet werden. Im Verlauf der Zellteilung und des aufwärtigen Wachstums der Mikro-Alge verzweigt sich eine Röhre aus rhomboedrischem Kalzit, die jede einzelne Zelle einschließt. Während der Verzweigung wird die optische Orientierung des Kalzites beibehalten. Das Aufwärtswachstum der Röhren geschieht durch Stapeln ringförmiger Laminae aus Kalzit um jede der einzelnen Zellen. Nach zahlreichen Zellteilungen und Verzweigungen der entsprechenden Kalzitröhren entstehen strauchförmige Einkristalle, die pro Jahr bis zu 10 mm Höhe erreichen können. Bei Lokalität 2 (Alpenzoo) verkalkt *O. stratum* in Form von Botryoiden sowie seitlich verschmolzenen Botryoiden aus faszikular-fibrösem Kalzit (ffK). Auf den Botryoiden sind die Einzelzellen im allgemeinen dichter gepackt als in den laminaren Biofilmen von Lingenau. Im Dünnschliff kann der *Oocardium*-ffK von abiotisch gebildetem ffK nur durch das örtliche Vorhandensein von Reliktstrukturen in ersterem unterschieden werden, wie sie beim Wachstum von *O. stratum*-Zellen entstehen. An beiden untersuchten Lokalitäten scheint sich *O. stratum* ausschließlich auf Kalzitkristallen anzusiedeln, die entweder im Substrat wie etwa Kalksteinklasten vorhanden sind, oder die vorher durch andere Biokalzifizierer gebildet wurden, oder die sich durch abiotische Fällung aus dem Quellwasser bildeten. Der Vergleich beider Lokalitäten zeigt, daß 'Oocardium-Tuff' oder 'Oocardium-Kalzit' kein einzelner, feststehender Typ von Mikrofazies ist sondern durch den Habitus des abiotischen Zements vor Ort angelegt wird. Ein vorläufiger Vergleich abiotischer Kalzitifällungsraten aus einer alpinen Halbhöhle mit beobachteten Raten der *Oocardium*-Verkalkung legt nahe, daß die *Oocardium*-Verkalkung um bis zu drei Zehnerpotenzen schneller erfolgt. Unsere Beob-

achtungen lassen es möglich erscheinen, daß manche Zementsteine in fossilen Riffen und scheinbar abiotisch gebildete Meeresboden-Präzipitate der geologischen Vergangenheit durch mikrobielle Verkalkung angelegt wurden.

1. INTRODUCTION

Limestones formed in association with cool springs are broadly reminiscent of post-2.4 Ga Proterozoic carbonates with respect to: (1) (microbial) biocalcification of induced type only, (2) absence of controlled biocalcifiers, and (3) formation of flowstones at the sun-lit surface of the deposit (Sanders et al., 2008). The widely variable chemistry of different carbonate-depositing cold springs represents a natural laboratory that allows controls over aspects of carbonate deposition to be tested without the constraint of the secularly changing chemistry of sea water. In our experience, in spring streams of the Alps, the most significant biocalcifiers include cyanobacteria, Zygnematophyceae (e. g. the desmid *Oocardium stratum*, the filamentous zygnemales *Mougeotia*, *Zygnema*), and diatoms. Further biocalcifiers, such as other Zygnematophyceae (e. g. *Cosmarium*) and Charophyceae s.s. (e. g. *Chara*, *Nitella*), xanthophycean algae, and mosses are of subordinate significance. Whereas cyanobacteria are well-known biocalcifiers, *O. stratum* is very rarely mentioned (Pen-tecot, 1991; Freytet and Verrecchia, 1998; Merz-Preiß and Riding, 1999) and is not discussed in recent summaries on microbial mineralization (see Ehrlich, 2002; Konhauser, 2007). Our data show that, at least in the Alps, microbially-induced calcium-carbonate precipitation from cold springs is much more widespread than that from thermal springs (Sanders et al., 2006a, b; Sanders et al., 2008; compare also Ford and Pedley, 1996). Wallner (1933, 1934a) showed that large quarried deposits of cold-spring associated limestone had been formed mainly by the desmid *O. stratum*. Possibly the publication of his findings in journals unrelated to geology hindered due appreciation of Wallner's pioneering work until recent times. In the present paper, the experimentally-controlled formation of *Oocardium* tufa is described in detail for two selected spring creeks situated in the Eastern Alps (Fig. 1). Each stream was investigated over years with a variety of methods (Table 1). Our results show that *Oocardium* tufa can grow in a seasonally-laminated style, at a rate attaining high rates of tropical shallow-marine carbonate production. The calcification of *O. stratum* is controlled by the habitus of the 'abiotic' cement formed at a spring site. '*Oocardium* calcite' is not a single type of microfacies, but embodies different microfacies that may look similar to abiotic cements. This potentially bears implications for the interpretation of cement reefs and apparently abiotic seafloor precipitates of the geological past.

1.1 BACKGROUND TO SPRING-ASSOCIATED LIMESTONE DEPOSITION

With respect to their total geographic extent, limestones deposited from cold springs are among the most widely distributed carbonate deposits on Earth (cf. Ford and Pedley, 1996). Individual deposits range from a few decimeters to more than

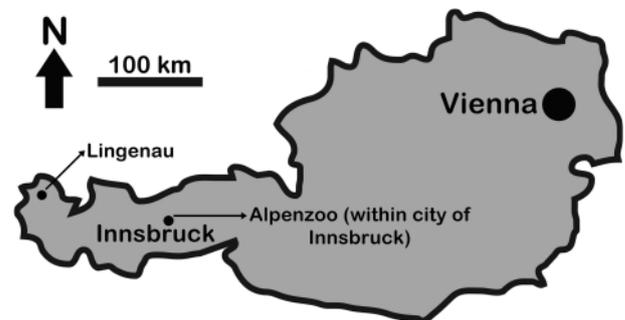
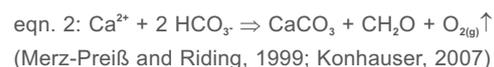


FIGURE 1: Geographic position of the spring creeks with active *Oocardium* calcification described in the present paper.

a kilometer in lateral extent, but most are in the size range of a few tens to a few hundreds of meters (Fig. 2). In the pH-range 6.5 to 8.5 of most limestone-depositing spring waters, precipitation and dissolution can be expressed as:



If carbon dioxide is removed (\uparrow), calcium carbonate precipitates. If carbon dioxide is added (\downarrow), calcium carbonate dissolves (Bathurst, 1975). After emergence of a spring, different physical processes such as pressure release, turbulence, and warming of the water withdraw CO_2 (\uparrow), with a consequent rise of calcium carbonate saturation state (Chen et al., 2004). Both HCO_3^- and CO_2 are also withdrawn by photosynthetic organisms, for instance, according to:



For net accumulation of spring-associated limestone is a high total concentration in both Ca^{2+} and HCO_3^- . 'Excess CO_2 ', although present in most limestone-depositing waters, is not indispensable to achieve supersaturation for CaCO_3 . Immediately downstream of spring emergence, limestone deposition at first tends to be low or absent because the water has to flow for some distance before supersaturation is sufficiently high by degassing of CO_2 (Fig. 2). Many springs are situated in a morphological depression, so the initial reach of the spring creek tends to flow over gentle slopes with low turbulence, slowing the degassing. Depending on spring discharge, local topography, and supersaturation for calcium carbonate, deposition of limestone diminishes farther downstream (Fig. 2). In most cases, however, the water still is weakly supersaturated for calcite, but further precipitation is prevented by kinetic factors (Berner and Berner, 1996).

1.2 GROWTH AND CALCIFICATION

Oocardium stratum thrives in aggregations of unicelled micro-

unicelled micro-algae. Commonly, each unicell is located atop of a 'tube' of mucilage surrounded by calcite (Fig. 3). In frontal view (the aspect with the longest axis), each unicell is characterized by a bipartite, heart-like shape with a minor median constriction (isthmus). In life, the longest axis of each unicell (=transapical axis) is positioned at right angle to its direction of growth (Golubic and Marcenko, 1958). Each unicell is typically positioned with about two-thirds to one half of its transapical axis within a tube of calcite that has been formed along the outer surface of the mucilage court of the unicellular micro-alga (Wallner, 1993, 1935a; Golubic and Marcenko, 1958). Each unicell is coated over its upper half by a cupolate halo of mucus reaching out of the tubular mucilage. The initial locus of formation of the calcite tubes is thus situated in the fringe where the mucus capsule abuts the calcite tube. After reproduction by vegetative cell division, the two mucilage tubes of the new cells calcify into slightly different directions upward. Upon cell division and 'branching' the calcite tubes that house each new unicell also branch. As the optical orientation of the calcite of the two new tubes is retained upon cell division and branching, large single calcite biocrystals produced by *O. stratum* may originate (Wallner, 1934a). Investigations of both fossil and active spring-limestone systems indicate that *O. stratum* can produce limestone deposits tens to hundreds of meters in lateral extent and decimeters to more than 10 meters in thickness.

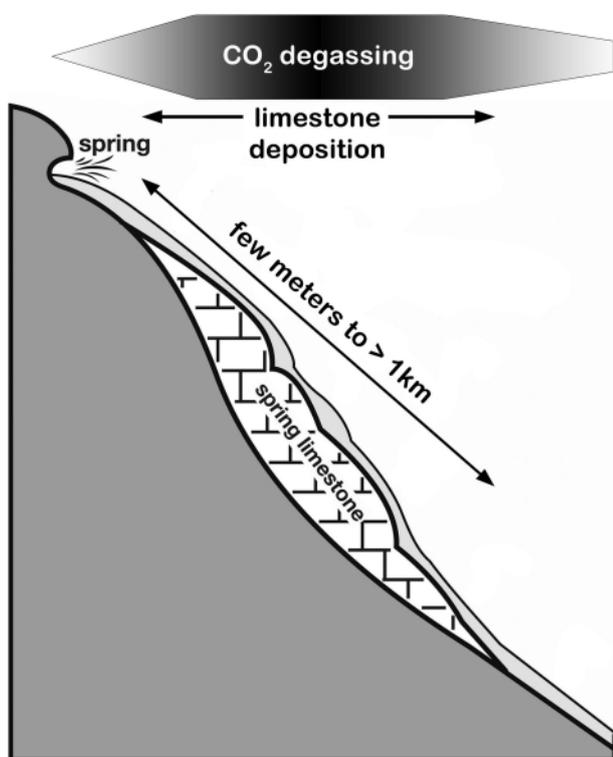


FIGURE 2: Generalized scheme of limestone deposition downstream of 'cool' springs at or close to saturation with respect to oxygen. Significant limestone deposition typically starts a short distance downstream of spring emergence, attains a maximum farther down, and ultimately tapers out when supersaturation for calcium carbonate has been sufficiently lowered. See text for further description.

2. GEOLOGICAL SETTINGS AND DEPOSYSYSTEMS

Lingenau: The active spring-limestone deposit of Lingenau (Fig. 1) is situated above a truncated succession of shallow-marine conglomerates, marls and sandstones of the Molasse Zone (Weissach Formation, Fig. 4A). Over most of its extent, the Weissach Formation is veneered by Würmian glacial till which, in turn, is overlain by a package 20–40 m thick of fluvial gravels (Rüf, 2006). The spring-limestone deposystem of Lingenau represents a perched-spring system (cf. Ford and Pedley, 1996) along the brink into a bedrock canyon, a typical position of spring limestones in the Alps (Sanders, 2001). The spring emerges by constant upwelling into a pothole about 50 cm in diameter. In the short, very steep reach above the upper waterfall (Fig. 5A), heavily calcified *Rivularia* and scarce *Oocardium* calcite are present. From the brink of the upper waterfall to the debouch of the creek into river Subersach, nearly the entire deposystem consists of *Oocardium* tufa (Figs. 5A and 6A). The *Oocardium* tufa consists of laminae typically 4–8 mm in thickness that are form-concordant with their immediate substrate, whether it is phytoclasts, lithoclasts, or spring limestone ('laminar' *Oocardium* tufa, Fig. 6B). Both in the upper and lower waterfall, sites of persistently intense water flow about 2–30 mm in depth are colonized almost entirely by *Oocardium*. Conversely, strips that are less intensely water-run and/or subject to seepage only are colonized by dark-brown to black tufts of the cyanobacterium *Scytonema* (Fig. 6A). The *Scytonema* tufts calcify in the form of 'loose' aggregates of calcitic, rhombohedral microspar to small-crystallite, rhombohedral calcite orthospar. Topographically higher above, and to the immediate west and east of the presently active limestone-depositing waterfall/creek-system, fossil tufa is present that is presently being eroded (Fig. 4A). Fossil waterfall tufas consist of form-concordant, subvertical laminae 3–8 mm thick of porous limestone that, in thin sections, is revealed as *Oocardium* tufa (see below for further description). Thus, at least the majority of the fossil waterfall tufas are of the same type as the one forming along the presently active deposystem. The fossil tufa deposits were nourished from springs fallen dry since an unknown period of time. The present limestone-depositing spring is moderately mineralized Ca-HCO₃ water (Table 2). The spring shows no marked seasonal change in discharge of an estimated 1–2 l/s. In 2005, bimonthly measurements of temperature, electrical conductivity, pH, and major cations, revealed overall low seasonal changes. Similarly, bimonthly measurements of δ¹⁸O of the water showed only a very small variation of less than 0.5‰ SMOW over the year (Rüf, 2006). In the modern spring creek, exclusively low-magnesian calcite of rhombohedral habitus is precipitated, also in association with *O. stratum*.

Alpenzoo: The spring that nourishes the Alpenzoo limestone deposit is situated in the Northern Calcareous Alps, in a belt of thrust slices on top of the Lechtal cover thrust nappe. The spring emerges just below the base of the Hötting Breccia, a lithified alluvial fan succession probably of Riss-Würm interglacial age (Fig. 4B; Penck, 1921; Paschinger, 1950; Sanders,

Method, Description	Approach, Techniques	Main goals, Remarks
Field documentation Field investigation, mapping of deposits, check of entire deposystem, sampling of facies types for slabs and thin sections	Deposits mapped on a scale of 1/2.000 on isohypsed satellite orthophotographs, and/or on laserscanned topography 1/2.000	(1) determine the extent of fossil, inactive, and active SAL deposits per occurrence, (2) map areal extent of different facies types
Experimental precipitation substrates Placement of diverse substrates for calcium-carbonate precipitation in active limestone-depositing creeks	Natural substrates: Formatted pieces of wood, brushes of natural fibers, loofah 'sponges', stones Artificial substrates: Cu-plates, steel nails, rinse fleece of plastic fibers, peeling 'sponges' of plastic fibers, steel-fibre meshworks	(1) Determine rates of precipitation on different non-living substrates, (2) determine 'calcification successions' within/on porous substrates (rinse fleece, loofah) (3) determine seasonality of precipitation rate and biotic assemblages Total observation interval for experimental substrates: five years (since 2003) for Lingenau, three years for Alpenzoo Check intervals of substrates: few weeks to more than a year
Thin sections Thin sections of fossil SAL and of SAL in active formation	Thin sections of SAL in active formation: samples dried and hardened with resin before cutting and polishing	Identify styles and rates of active calcification, and its 'translation' into fossil deposits
X-ray diffraction Diffraction patterns of powdered mineral samples of SAL deposits	Standard X-ray diffraction X-ray with Parallel-Beam Technique (PBT)	(1) Determine bulk mineralogy and carbonate polymorphism, (2) determine relative proportion aragonite/calcite, (3) determine mole% Mg in magnesian calcite (PBT)
Microbotanical investigation	Samples taken <i>in vivo</i> in the field, transported to lab in ambient water in a coolbox Investigation of entire sample and of cut-off sub-samples (some sub-samples stained with methylene blue) under (a) reflected light, (b) transmitted light, (c) polarized light, (d) dark-field microscopy	(a) Taxonomic composition of macro- and microbiota, (b) identification of early-formed calcium-carbonate crystallites and their relation to microbes
Electron microscopy SEM (backscattered-electron microscopy) Critical-point-SEM microscopy (CP-SEM)	SEM: (a) investigation of dried and sputtered samples formerly populated by living microbial assemblages, (b) investigation of samples cleared with H ₂ O ₂ from their microbial population CP-SEM: investigation of samples of actively-forming microbialite taken <i>in vivo</i> in the field, and with their microbial assemblages still in place	(a) investigate forms and habitus of microbially-induced calcium carbonate, (b) determine the relation of microbes to their calcium-carbonate precipitates Conducted mainly for limestones forming in association with <i>Oocardium stratum</i> , <i>Rivularia</i> , <i>Scytonema</i> and diatoms
Investigation of physico-chemistry of limestone-precipitating spring waters	Measurement of (a) <i>in-situ</i> : temperature, electrical conductivity, pH, alkalinity, (b) major cations and anions, (c) free CO ₂ , (d) oxygen saturation, of active limestone springs, by: (a) transportable multi-parameter detectors (T, pH, cond), by Aquamerck® alkalinity titration in the field, (b) AAS, ICP, autoanalyzer, (c) titration (CO ₂), (d) titration (oxygen saturation) Water samples for cations were spiked with three drops of 5% HNO ₃ Unspiked water samples for anions or for complete kat-an analyses were transported in a coolbox	Determination of (a) physico-chemistry of spring waters that precipitate calcium carbonate and, in a few cases, other compounds (e.g. iron oxide) (b) seasonal physico-chemical gauge of limestone springs (in case of repeated measurements)

TABLE 1: Methods used to investigate springs and the associated limestones. Abbreviations: AAS=Atomic absorption spectrometry; ICP=Inductive coupled plasma spectrometry; SAL=Spring-associated limestones.

2008). In the area of spring emergence, the Hötting Breccia overlies either a glacial lodgement till of probable Riss age (Fig. 4B) (Ampferer, 1914) or, where the till is absent, an intensely deformed succession of dolostones and cellular dolomites that probably belongs to the Lower Triassic Reichenhall Formation. The spring was captured decades ago for water supply of the nearby 'Alpenzoo' park. Today, only a reduced part of the original discharge (approximately 5–10 l/s) emerges from a concrete tube a few meters downslope of the former natural site of emergence. Farther downstream, relict deposits of spring limestone, that present undergo erosion by the creek, suggest that the reduction of discharge due to spring capture led to a reduction in the extent of limestone deposition. Furthermore, about 150 meters downstream of spring emergence, isopachous calcite cements within periglacial fluvial conglomerates ('Deltaschotter beim Engländergab'; Patzelt and Resch, 1986) had yielded a U/Th cementation age of 3000 ± 500 a (Fig. 4B) (Ostermann, 2006). The young age of the calcite cements is explained by some 20 meters of erosional incision of the spring-creek since cementation. This, and the entire geomorphic context of the creek within an incised small valley (Fig. 4B), implies that the net geomorphic action of the limestone-depositing creek was incision, not aggradation. Along the *present* extent of the creek, in its upstream part, limestone deposition takes place in a very-steeply dipping system composed of moss tufa (Fig. 5B). The moss-tufa reach consists of subvertical steps of moss tufts (mainly *Palustriella commutata*, *Eucladium verticillatum*) separated by gently-dipping to flat terraces of moss riddled by small ponds herein dubbed 'nymph ponds'. In the nymph ponds, the water of the creek that descends mainly within the megapore space of the tufa limestone below the moss tufts becomes re-emergent. Within and along the rims of the nymph ponds, calcifying tufts up to 10 cm thick of *Scytonema*

are present. Microbotanical and SEM investigations indicate that, in the Alpenzoo creek, the moss itself is insignificant in calcification. Instead the moss tufts provide a large surface for settlement of calcifying micro-organisms such as *Oocardium*, diatoms, and cyanobacteria (*Rivularia*) (Willegger, 2008). Downstream of the moss-dominated upper reach, calcification of the wetted perimeter of the main channel is dominated by *Oocardium* and *Rivularia*, without or with moss (Fig. 5B). *Oocardium stratum* grows and calcifies in form of hemispherical 'pustules' typically between 1–5 mm in diameter (Fig. 6C). Although the pustules may locally merge into short laminae, no pervasive laminar growth of *Oocardium* tufa comparable to Lingenau was observed. Farther downstream, *Oocardium* disappears whereas the presence of *Scytonema* and *Rivularia* continues for a few meters in decreasing intensity of calcification down to nil. The Alpenzoo spring sheds a moderately mineralized Ca-(Mg)-sulphate water. The variations in major physico-chemical parameters are in a similar range as the spring of Lingenau. Within the Alpenzoo creek, besides of micrite, microspar and micropeloids of low-magnesian calcitic mineralogy, fascicular-fibrous calcite (ffC) is formed. The ffC is most obvious in isopachous fringes of cement that are formed by 'abiotic' precipitation, but can also be induced by calcification of *O. stratum*.

3. CALCIFICATION OF *O. STRATUM*

3.1 LINGENAU

At Lingenau the most conspicuous feature of both the active and the fossil *Oocardium* tufa is lamination (6B). Individual laminae typically range 4–8 mm in thickness, and are form-concordant with respect to their substrate. In thin section, each lamina consists of an array of elongated, 'bush-shaped' crystals of calcite, with each crystal extending over the entire thickness of a lamina (Figs. 6B and 6D). Each of the bush-shaped crystals starts from a point at the substrate and widens up-section. In pristine *Oocardium* calcite, each 'branch' of a calcite-crystal 'bush' is centered by a tube-shaped hollow typically between 15–25 microns in width. Very little variation is seen in the overall form of the bush-shaped calcite crystals, and the thickness of calcite branches and diameter of the tubes within. Up-section, the described laminae are terminated along a truncation surface. The surface is overlain either by the next lamina of *Oocardium* calcite as described, or by a very thin lamina of microsparite. Microbotanical preparations of active *Oocardium* tufa show that each branch of the described calcite bushes is topped by a single cell of *O. stratum*, i. e. the branches are unequivocally produced by calcification of the micro-alga (cf. Fig. 3). In SEM, the uppermost parts of the crystal branches show a subcircular cross-section. A few tens of micron farther down, however, crystal surfaces characteristic of rhombohedral calcite appear at the surface of the branches, and the outer diameter of the branches thickens. The initial stage of growth of *O. stratum* was inspected on phytoclasts (e. g. leaves, bark) that

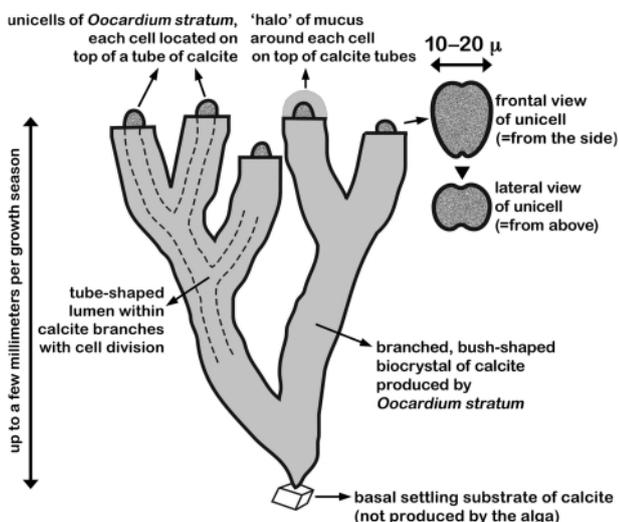


FIGURE 3: Main external features of cell and growth of *Oocardium stratum* in rhombohedral-calcitic habitus of crystallization (modified after Wallner, 1933; Golubic and Marcenko, 1958). The growth season of *O. stratum* corresponds approximately to the well-lit season from April to October.

were covered by just a 'hue' of calcium carbonate. In these cases, *O. stratum* seemed to settle exclusively on pre-existing crystals of rhombohedral micro- to orthospars; these calcite crystals grew in direct contact with the natural substrate (Fig. 6E), and were also observed in absence of initial *Oocardium* growth. Both in microbotanical preparation and in SEM, the basal calcite crystals showed no evidence for a biological induction on their formation, that is, they seem to have formed by 'abiotic' precipitation. The short, tube-shaped calcite crystals that represent the very early growth stage of *O. stratum* grow upward by addition of ring-shaped laminae of calcite along the contact of the mucus hood the algal cells are capped by and the calcite tube below (Fig. 3). Farther down the calcite tubes, however, the surfaces of the calcite rhombohedron overall become more developed, and the outer diameter of the calcite tubes thickens (Figs. 6F and 6G).

We conducted experiments to test whether the lamination of

the tufa is of seasonal origin, and to investigate the calcification rate of *O. stratum*. Porous rinse fleece of plastic fibres were placed in early spring at several locations along the creek. In addition, formatted rods of wood, two peeling sponges consisting of a tuft-shaped, highly porous plastic tissue, and two copper plates were placed. In autumn, one peeling sponge (the other had been lost) was coated by a layer up to 10 mm in thickness of *Oocardium* calcite (Fig. 6H). After more than one year, the steel nails fixing the substrates were also encrusted by *Oocardium* calcite. The copper plates remained uncovered for more than one year, but then became embedded in the *Oocardium* calcite by lateral overgrowth from the pristine *Oocardium* tufa. The most conclusive experiments were those with rinse fleece. In autumn, after nearly eight months, each rinse fleece was coated by a lamina approximately 8 mm in thickness of *Oocardium* calcite (Fig. 7). In late autumn, calcification of *Oocardium* seems to have been

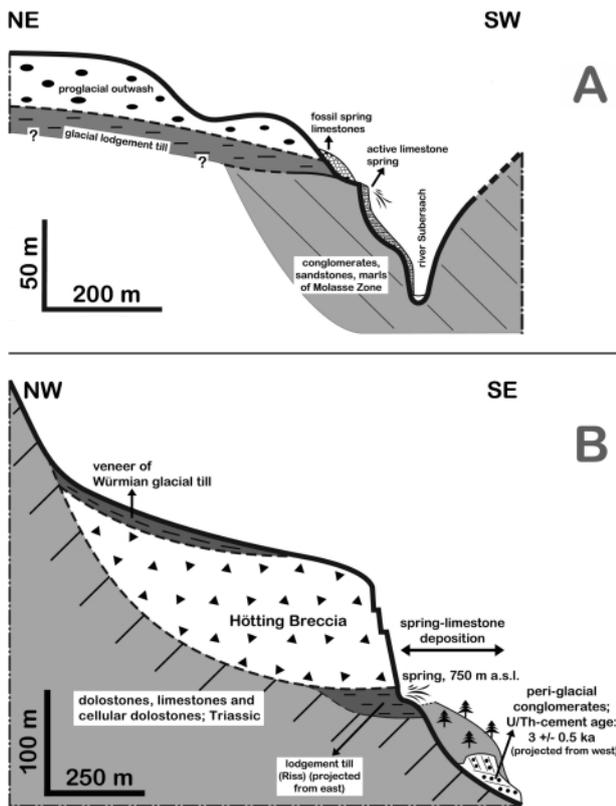


FIGURE 4: Simplified sections of geological settings of described spring-limestone deposystems (vertically exaggerated). A: At Lingenau (Vorarlberg), a truncated succession of the Molasse Zone is veneered by glacial till, followed up-section by proglacial fluvial gravels and sands. The presently active deposystem is nourished by a spring at the upper brink of the incised gorge of river Subersach. Fossil spring limestones are exposed both laterally aside and topographically above the active system. B: Adjacent east of Alpenzoo (Innsbruck, Tyrol), a truncated succession of folded and thrust dolostones, limestones and cellular dolostones of Triassic age is overlain by glacial lodgement till of probable Riss age, and/or by a lithified alluvial fan succession (Hötting Breccia; probably Riss-Würm interglacial). The limestone-depositing spring emerges closely below the base of the Hötting Breccia, and sheds into a small incised valley. Along the western flank of the small valley, a cemented succession of periglacial deltaic conglomerates is exposed. See text for further description.

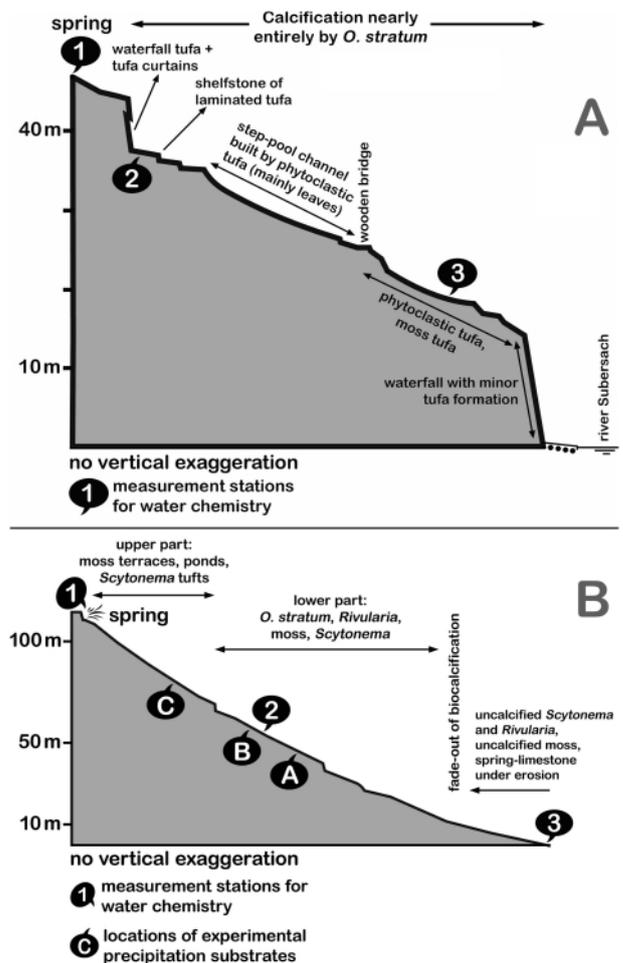
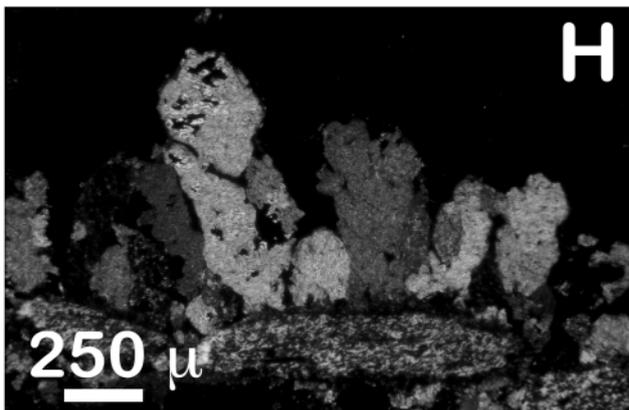
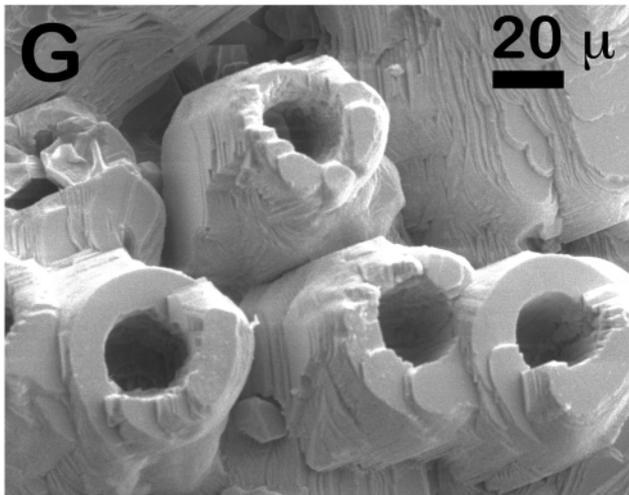
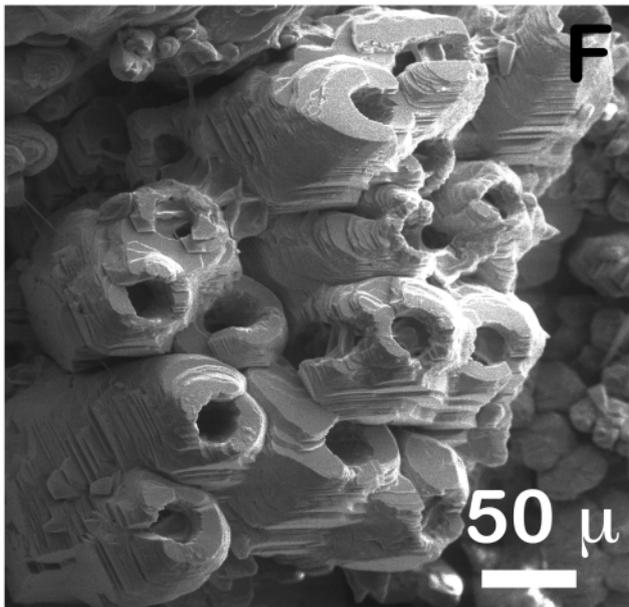
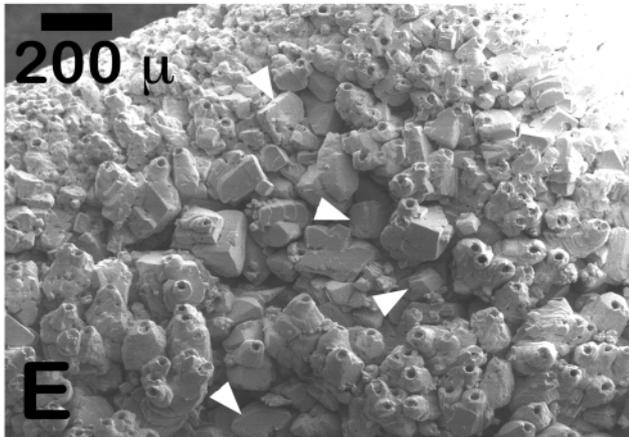
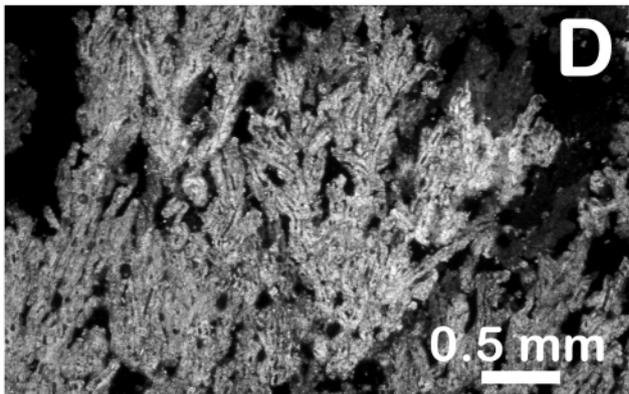
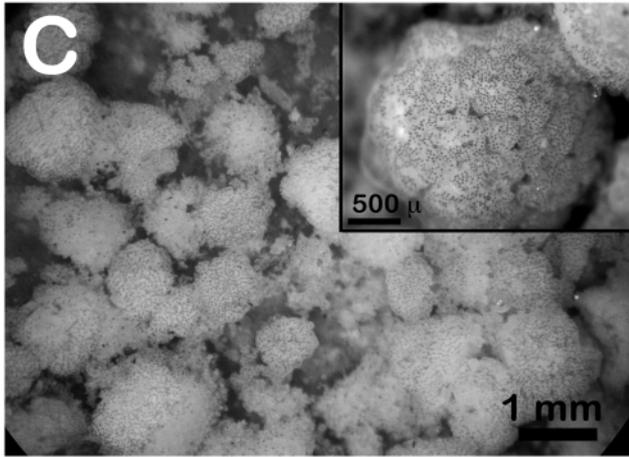
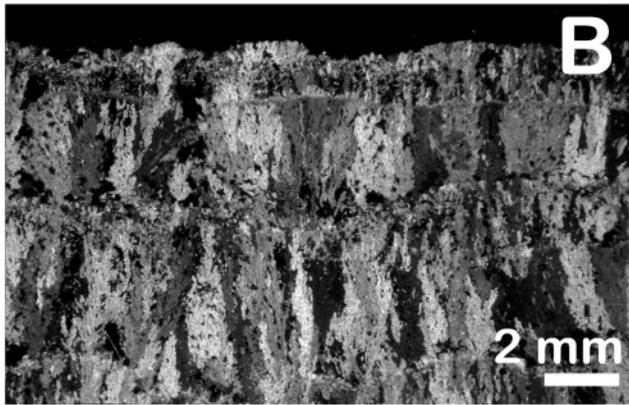
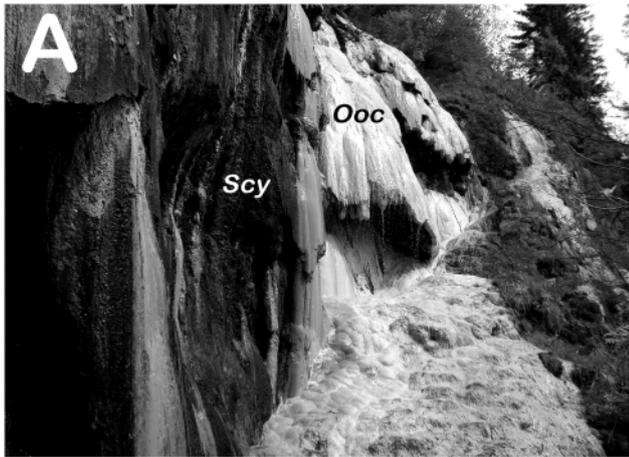


FIGURE 5: Sections along the spring-limestone deposystems. A: At Lingenau, almost the entire calcification proceeds in association with *O. stratum*, in fabrics of pure *Oocardium* tufa and, subordinately, in phytoclastic tufa and moss tufa. B: The upper part of Alpenzoo creek is characterized by a very steeply-dipping reach of moss tufa. In the lower part of the limestone-depositing reach, moss tufts are less common, and calcification proceeds in a stream bed paved by *Oocardium* tufa and by calcifying *Rivularia* and *Scytonema*. Still farther down, biocalcification fades out, and the geomorphic regime of the stream is erosional incision.

Contrasting styles of calcification by the micro-alga *Oocardium stratum* Naegeli 1849 (Zygnematophyceae) in two limestone-precipitating spring creeks of the Alps



reduced by spread-out of diatom mats directly above the *Oocardium* calcite. In the mucilage of the diatom mats, rhombohedral calcite crystals grew. In many cases, individual diatom frustules provided the center of a calcite crystal. Observation of calcified rinse fleece over several years indicates that the diatom mats, in turn, disappeared during spring, and growth of *O. stratum* started again above the older lamina of *Oocardium* calcite (Fig. 8). At sites of copious water supply, such as along the walls of runoff channels in the tufa limestone and at impact sites of water threads, the *Oocardium* calcite is transformed into a tough, dense, limpid, coarse-sparry cementstone (Fig. 9A). The cementstone is characterized by a 'rugged' outline of crystal boundaries, an irregular distribution of crystal size (not resulting from free crystal growth into water), an irregular-elongate shape of crystals, patches with diagnostic fabrics of *Oocardium* calcite, and an overall gradual downward transition from the surficial cementstone into unequivocal *Oocardium* calcite farther below (Figs. 9A – D).

3.2 ALPENZOO

Along the Alpenzoo creek in winter, parts of the stream bed can be yellowish to light-brown due to prevalence of diatom mats. For most of the year, however, the stream bed shows green hues because of the presence of *O. stratum*. The 'pustular' calcification of *O. stratum* in Alpenzoo creek is distinct from the bush-like style at Lingenau not only with respect to

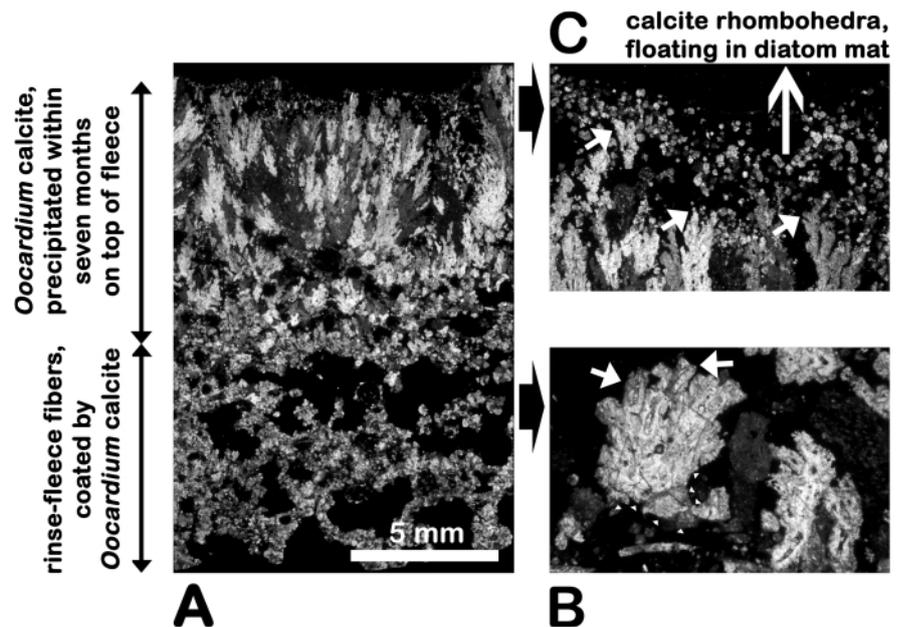


FIGURE 7: Calcification of a rinse fleece of plastic fibers placed for seven months, over the well-lit season, in Lingenau limestone-depositing creek. A: Within the pore space of the fleece, *O. stratum* settled on the plastic fibers and started to calcify (subfigure B). Upon early calcification on the fleece, and upon calcification of the 'winner' *Oocardium* settled on the upper surface of the fleece, the pore space became too dark for further growth, and the 'loser' *Oocardium* settled in the pore space died. The 'winner' *O. stratum* on the upper, day-lit side of the fleece continued to grow and calcify over the well-lit season. During October to November, growth and calcification ceased, and the *Oocardium* aggregate became terminated and overgrown by a diatom mat (subfigure C). Crossed nicols. B: *O. stratum* settled within the pore space of the rinse fleece, and died in a juvenile stage of development. Note typical 'inverted-cone' shape (outlined by small white triangles) of initial *Oocardium* calcification, and the first few branches of *Oocardium* calcite (highlighted by white arrows; see also Fig. 3) produced by the first few cell divisions. Width of view 1.6 mm. Crossed nicols. C: Termination of growth and calcification of *O. stratum* at the end of the well-lit season (a few tops of *Oocardium* calcite indicated by white arrows), and calcite rhombohedra floating in the extracellular mucus of a diatom mat above (diatoms are too small to be visible at this magnification). The diatom mat established in rise of the low-lit season. Width of view 4 mm. Crossed nicols.

external shape. In the pustular growth style, groups of cells of *O. stratum* are situated close to each other, resulting in a dense hemisphere of calcite reminiscent of a botryoid of abiotically-precipitated cement (Fig. 6C). As mentioned, in the Alpenzoo creek, both pore-fringing cements (Fig. 9E) and the *Oocardium* calcite formed at surface are fascicular-fibrous calcite. The tubes of *Oocardium* ffc consist of bladed calcite

FIGURE 6: A. Upper waterfall at Lingenau (cf. Fig. 5A). The light strips labelled Ooc in the waterfall are overrun by a layer approximately 3 - 20 mm thick of water, and are entirely colonized by *O. stratum*. The dark strips labelled Scy are only wet by seepage, and are colonized by *Scytonema*. At the toe and ahead of the waterfall, shelfstones of tufa limestone are present. B. Thin section of laminated tufa formed at Lingenau. The laminae are form-concordant with respect to shape and steepness of their substrate. The waterfall tufa shown in Fig. 6A consists of tufa limestone as shown. Each lamina of tufa consists of large biocrystals precipitated by *O. stratum*. Crossed nicols. C. Hemispherical 'pustules' of *Oocardium* calcite in Alpenzoo creek. Tiny grey sparkles on white pustules are individual unicells of *O. stratum*. This style of *Oocardium* calcification is characteristic of Alpenzoo creek. D. Thin section of *Oocardium* calcite at Lingenau. The calcite consists of large, branched, bush-shaped biocrystals wherein each branch is originally centered by a hollow tube (=the space occupied by the *Oocardium* unicells during growth). Crossed nicols. E. SEM image of initial calcification of *Oocardium* on a leaf of *Salix*. Before settlement of *O. stratum*, the leaf became coated by a thin crust of rhombohedral calcite (a few crystals denoted by white arrowtips). On this crystal pavement, cells of *O. stratum* had settled and began to calcify upwards. F. Same SEM sample as shown in Figure 6E. In upward calcification, *O. stratum* forms a mucilage model appearing as hollow tubes coated by calcite. The calcitic tubes grow by stacking of calcite laminae. Note identical orientation of rhombohedron surfaces in the field of view (0.325 mm), comprising every tube of *Oocardium* calcite. G. SEM view of tips of tubes of *Oocardium* calcite, as in Figure 6F. Note progressive widening of crystal surfaces of the calcite rhombohedron downward from the upper tip of tubes. H. Detail of calcification from a peeling sponge of plastic fibers. Crystals of *Oocardium* calcite in initial stage of upward growth. Note distinct optical orientation of crystals. Upon progressive calcification of the tissue of the peeling sponge, darkening of the pore space of the peeling sponge stopped *Oocardium* growth in an initial stage. Crossed nicols.

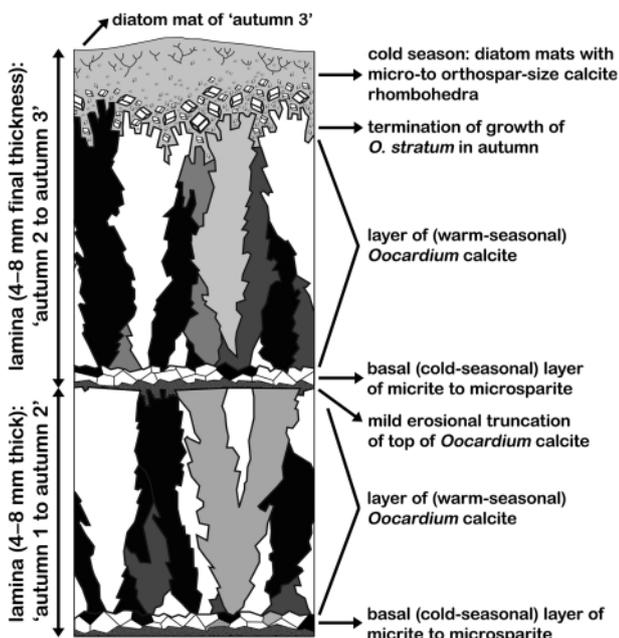


FIGURE 8: Seasonal layering of laminar *Oocardium* tufa composed of rhombohedral calcite. During the low-lit season, each lamina of *Oocardium* calcite formed over the previous well-lit seasons growth may become slightly truncated, and/or is overlain by a thin lamina of micrite to microsparite. Different shadings highlight individual biocrystals of *Oocardium* calcite as seen under crossed nicols.

fibers oriented parallel or at an acute angle relative to upward growth direction (Fig. 9F). As a result, the upper termination of the *Oocardium* calcite tubes shows a dog-toothed outline shaped by the upward-growing calcite fibre crystals (Figs. 9F and 9G). In addition, the upward-growing calcite fibers are of smaller diameter closely adjacent to the mucus halo of *O. stratum* and become of larger diameter towards the outer perimeter of the calcite tube, or towards the competitive surface formed along the contact with the calcite tube of a closely adjacent *O. stratum* cell (Fig. 9H).

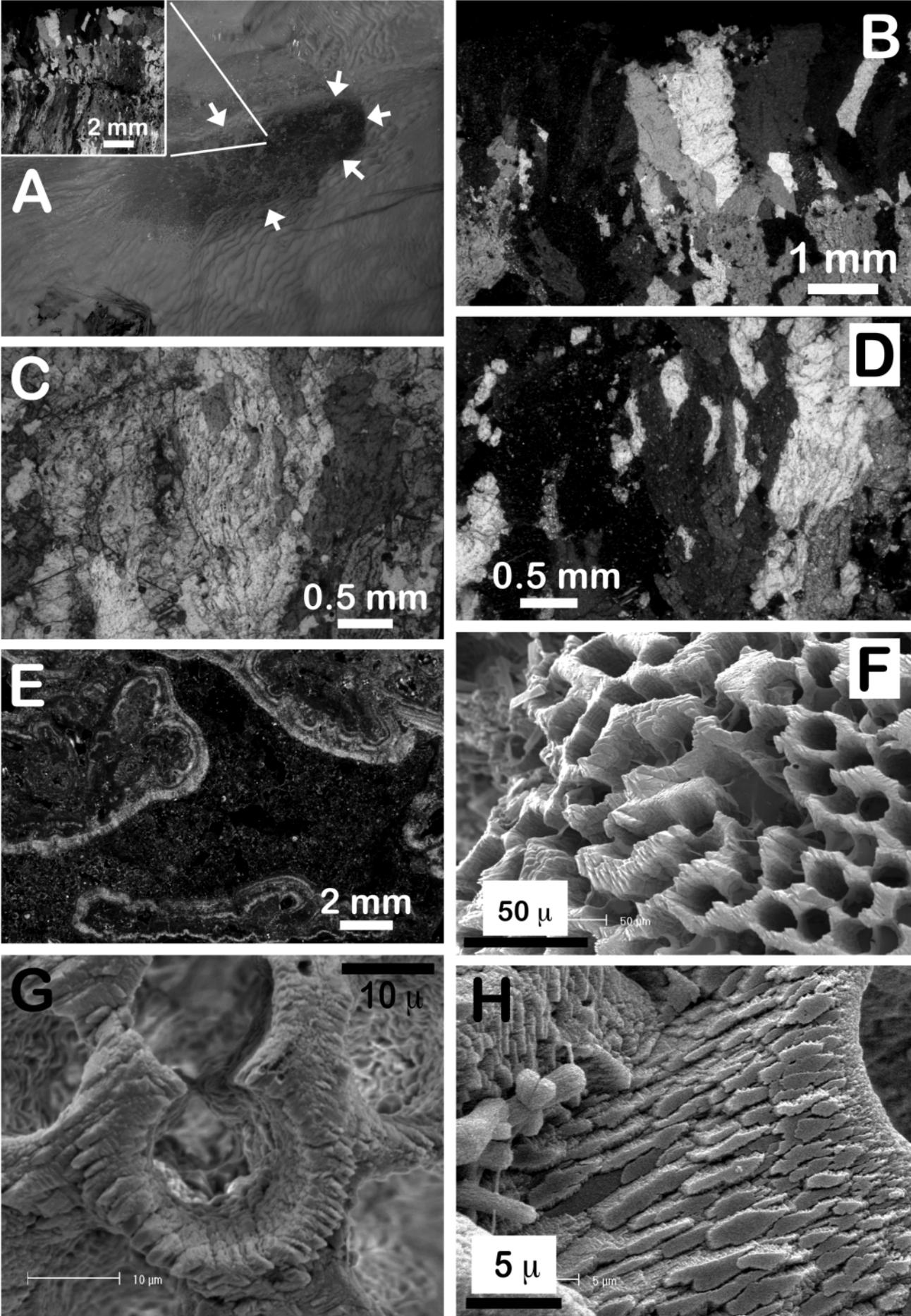
Field experiments were conducted over several years using diverse precipitation substrate, including rinse fleece of plastic fibers, loofah, a brush of natural fibers (placed within the moss tufa in the upper part of the deposystem), and copper plates. Both the rinse fleece and the loofah remained uncalcified over more than a year. After placement for more than one year within the creek, thin sections of fleece and loofah showed just small patches of micropeloidal grainstone formed mainly by trapping in the pore space of fleece and loofah; the

day-lit surface, by contrast, remained uncalcified and was not overgrown by organisms. Only during the successive well-lit season (spring to early autumn), the appearance of fleece and loofah changed rapidly: their upper surfaces became colonized by calcifying tufts of *Rivularia*, pustules of *Oocardium* calcite, tufts of *Scytonema* and, subordinately, filamentous zygnematalean micro-algae (Fig. 10). The dark underside of the experimental substrates had been cemented to the bottom with a fringe of fascicular-fibrous calcite. At this stage, the rinse fleece and the loofah could barely be distinguished from the adjacent, natural limestone-encrusted stream bed. The rate of calcification on the experimental substrates is very low in relation Lingenau. A few pustules of *Oocardium* calcite grew to a size of about 2 mm over two years, but most were only up to 1 mm in diameter (Figs. 10 and 11 A – C). Surprisingly, the brush of natural fibers placed in the moss tufa remained completely uncalcified and devoid of any organic overgrowth over more than three years instead. The brush is gradually being covered by lateral overgrowth from uncalcified *Palustriella commutata*.

3.3 INTERPRETATION

The style of growth and laminar calcification of *O. stratum* at Lingenau is closely similar to that described by Wallner (1933, 1934a) for tufa deposits in Bavaria. Wallner (1935a, b) had noted that *O. stratum* seems to settle only on substrates of calcium carbonate, and all our observations and field experiments further corroborate this (see below for discussion). Experiments on settling and calcification of *O. stratum* led Wallner (1934b) to conclude that, in its calcifying state, the alga can template its calcification from a wide variety of low-magnesian calcitic material; the only prerequisite for calcification of *Oocardium* seems to be that the diameter of the 'initial seed crystal' on which the alga settles is of equal to larger diameter than the algal unicell (Wallner, 1934b, p. 262 f.). In the laminar *Oocardium* tufa of Lingenau, the different optical orientations combined with the large size of the bush-shaped calcite crystals indicate that the original orientation of the calcite crystal lattice is retained upon cell division. SEM inspections suggest that the initial orientation of the crystal lattice of *Oocardium* calcite is templated from a crystal of the abiotic calcite substrate the single 'initial' alga had settled on, and then is inherited over many cell divisions during upward growth. The seasonal laminations indicate that calcification

FIGURE 9: A. Impact patch (grey area delimited by white arrows) of water thread at the toe of the upper waterfall at Lingenau (see Fig. 6A). Towards the impact site, *Oocardium* tufa with micro-terraces grades into a very tough, limpid, light-brown, cementstone crust (delimited by white arrows). Inset in upper left: In thin section, the crust is a calcite cementstone 2 – 4 mm in thickness. Down-section, the cementstone grades into *Oocardium* calcite as described. Crossed nicols. B. Detail of cementstone crust shown in preceding photo. Note crystal boundaries of 'rugged' outline, and the presence of small patches of calcite crystals between much larger crystals. Crossed nicols. C. Detail of cementstone crust shown in Fig. 9A. Within the dense cementstone, diagnostic relicts of *Oocardium* calcite as described are present. Parallel nicols. D. Same as Fig. 9C, but crossed nicols. E. Photomicrograph of tufa limestone of Alpenzoo creek, about 4 cm below the actively-forming tufa on the stream bed. An initial fabric of tufa limestone formed mainly by micritic calcification is overlain, towards the macropore space, by an isopachous fringe of fascicular-fibrous calcite (ffC). The macropore space is filled by a fenestral peloidal to micropeloidal grainstone. Crossed nicols. F, G. SEM images of surface of botryoid of *Oocardium* calcite as typical for Alpenzoo creek. Calcification proceeds in form of fascicular-fibrous calcite. Note acute terminations of individual calcite fibers alongside the tubes left by *O. stratum* cells. H. SEM image of the margin of a tube of fascicular-fibrous *Oocardium* calcite, Alpenzoo creek. The area of the growing surface of individual crystal fibers becomes overall larger with increasing distance from the tube inhabited by a cell of *O. stratum*.



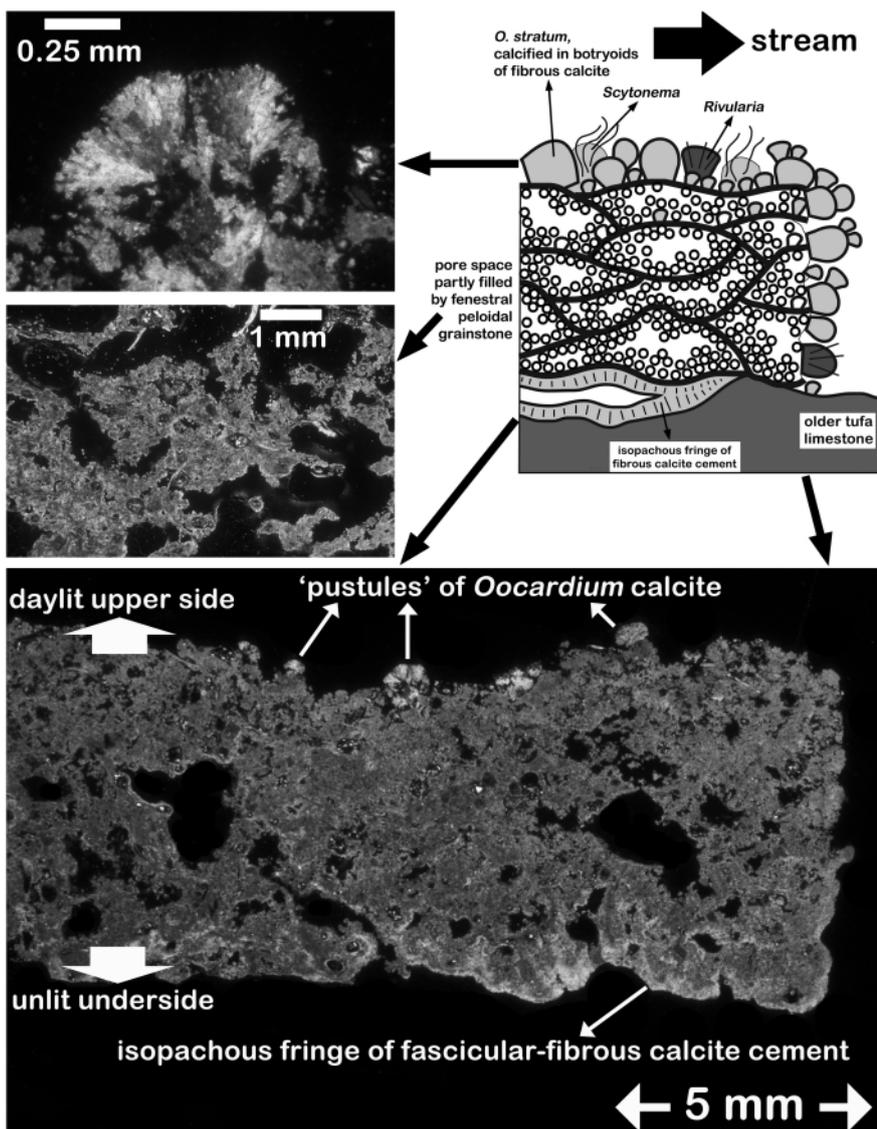


FIGURE 10: Pattern of colonization of rinse fleece of plastic fibers (heavy black lines in line-drawing) over two years in Alpenzoo limestone-depositing creek, Tyrol. See text for description and discussion.

induced by *O. stratum* stops or is strongly reduced in autumn and winter despite a number of green cells persist almost all year round, at least in the Alpenzoo creek. We found in both SEM and in wet micropreparations of *Oocardium* calcite: (a) the appearance of wider calcite-rhombohedral surfaces a few tens of microns down-section from the upper terminus of the calcite tubes, (b) the calcite walls of the tubes tend to thicken downward while the diameter of the inner lumen occupied by the mucus stem of the alga remains constant, and (c) in older/lower portions of *Oocardium* calcite bushes the inner lumen occupied formerly by the mucilage stems tend to be clogged by calcite - all this indicates that the initial biocalcification mediated by *Oocardium* is followed closely by abiotic precipitation of calcite. For the crusts of limpid cementstone of coarse-sparry calcite that form at sites of copious water supply, the prevalence of 'rugged' crystal boundaries, an irregular distribution of crystal size, an irregularly elongated shape of crystals, patches with diagnostic fabrics of *Oocardium* calcite,

and an overall gradual downward transition from the surficial cementstone into unequivocal *Oocardium* calcite farther below all indicate that these cementstones form from original *Oocardium* calcite by (a) recrystallization (to largely obliterate the diagnostic original fabric) combined with (b) a significant amount of further, abiotic crystallization by water percolating the pore space. For cementstone fabrics that originate by a combination of, both, recrystallization and significant further abiotic crystallization, the term 'combispar' is here-with proposed.

For both sites, it seems likely that the seasonality of calcification is related to increased diatom growth and reduced *Oocardium* growth in winter. The different styles of *Oocardium* calcification, however, are more likely related to water-chemical conditions than to genetically disposed differences in biocalcification of different *Oocardium* ecomorphs. In view of the differences in water chemistry and abiotic calcite precipitates of both springs, the most probable explanation is that the calcification habitus of *O. stratum* is dictated by the form of the abiotic cement at site. Under abiotic conditions, ffC and similar fibrous CaCO_3 precipitates form fans, botryoids, and fringes of laterally-merged botryoids (e. g. Tucker and Wright, 1990), similar to the *Oocardium* calcite along Alpenzoo creek. The field experiments in Alpenzoo creek indicate that on both types of precipitation substrates (rinse fleece, loofah) the ground needed to be prepared before settlement and calcification of cyanobacteria and algae. Ground preparation proceeded mainly by trapping and binding of micropeloids into small aggregates of grainstone along the tissue fibers of the fleece and the loofah. The micropeloids were probably passively swept into, and trapped within, the tissue of the fleece; another part of the micropeloids may also have formed directly within the fleece tissue by calcification of unspecified bacteria. Relative to the rate of colonization-calcification of identical rinse fleece at Lingenau, in Alpenzoo creek this first stage of ground preparation took much longer, about two years. Over this entire interval, at their surface both the fleece and the loofah remained uncalcified. Thus, ground preparation for colonization seems to have proceeded from within the tissues towards

the surface. Once the tissue's pore space was sufficiently (but still incompletely) clogged by lime sediment, colonization and calcification started during a single spring. The active pustules of *Oocardium calcite* had calcified to a maximum length of about 1.5 mm. This indicates that the rate of calcification along Alpenzoo creek is much lower than at Lingenau. The complete absence of calcification of the brush of natural fibers placed in the upper, moss-dominated part of the deposit remains enigmatic. The physical conditions at the site of the brush should be conducive to calcium-carbonate precipitation. Before approach the brush, however, the water had by-passed abundant moss tufts and the large pore space within the moss tufa. We therefore tentatively suggest that the upper, green parts of mosses release substances preventing precipitation of calcium carbonate, and/or that in by-passing the pore space of the moss tufa the water became of a lower saturation state from uptake of CO₂ from oxidation of organic matter.

4. DISCUSSION

Our results show that '*Oocardium calcite*' is not a single type of CaCO₃ precipitate but may acquire different crystal habituses that probably are steered by spring-water chemistry at site (Fig. 12). The hydrological regime at the site of growth also influences calcification. As outlined, under copious supply of water that yet allows for growth of *O. stratum*, calcification tends to be more intense, resulting in low-porous *Oocardium* tufa and/or in formation of coarse-grained *Oocardium* combisparstone. Because the annual temperature change of the two investigated springs is only about 3°C (Table 2), it is probably the seasonal change in light regime (day length, angle of irradiation) that steers appearance-disappearance of *O. stratum*. The spring waters of both Lingenau and Alpenzoo are only moderately charged with dissolved major cations and anions. With respect to its major anionic and cationic composition, the water of Lingenau is near the upper limit allowed for the chemical composition of drinking water (cf. Högl, 1980; Zötl and

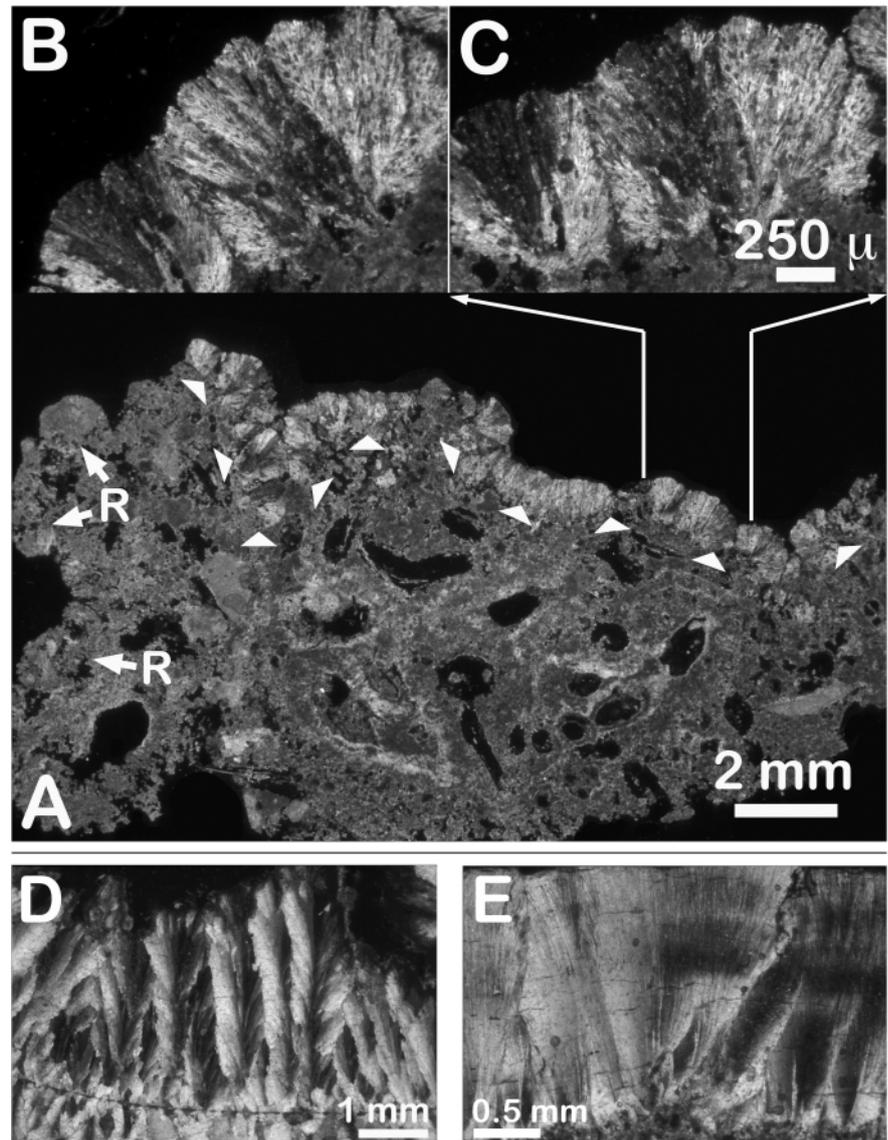


FIGURE 11: A – C. Thin-section of calcified loofah in Alpenzoo creek. A: The pore space between phytomoulds is mainly filled by peloidal to micropeloidal grainstone. On the surface, a fringe (denoted by white arrowheads) of laterally-merged botryoids of *O. stratum*, and tufts of calcifying *Rivularia* (arrows labelled R) established. Crossed nicols. B, C: Detail of fringe of botryoids of fascicular-fibrous *Oocardium calcite*. Upon clockwise turning of the microscope stage (from B to C), the extinction in the fibrous calcite runs counterclockwise. Crossed nicols. D: Thin-section of fascicular-fibrous calcite grown upward from a crystal fringe formed previously along a water table (thin grey line in lower part of photo) within an open joint below day-lit surface. Note typical 'branching' of calcite fibers out from a median axial plane. Sample from fossil calcium-carbonate mineralization in open joints in gneiss, Laas, Southern Tyrol, Italy. Crossed nicols. E: Thin-section image of a fringe of fascicular-fibrous calcite precipitated within the pore-space of a breccia (Laas, Southern Tyrol, Italy). Crossed nicols.

Goldbrunner, 1993). At other limestone-precipitating springs with significantly higher total concentrations of dissolved ions (unpubl. data), *O. stratum* is absent. This may suggest that *O. stratum* prefers well-lit waters of low- to moderate-concentration of major cations (Ca, Mg, bicarbonate, sulphate). To date, however, not enough data on the chemical, hydrological, photic and temperature regime of *O. stratum* are available to allow for definite conclusions on its presence. We have observed small calcified pustules of *O. stratum* even at springs that are otherwise not limestone-precipitating. This emphasizes the high capacity of this micro-alga for calcium-carbonate

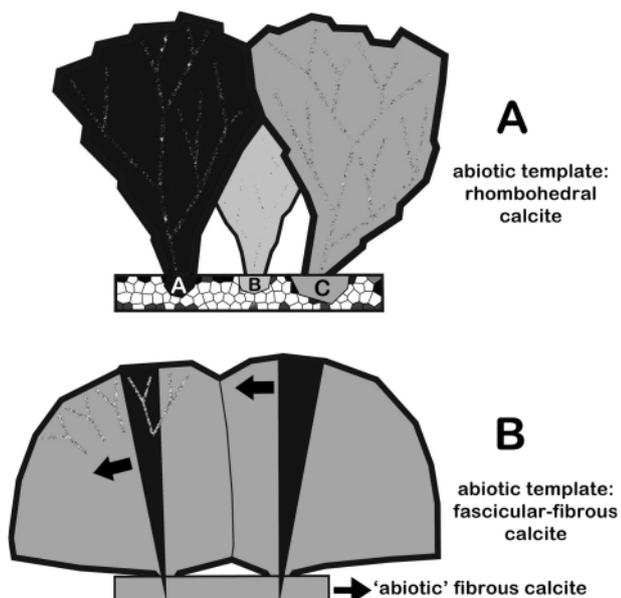


FIGURE 1 2: Calcification of *O. stratum* as a result of the habitus taken by the abiotic cement at site. A: 'Lingenau pattern', and B: 'Alpenzoo pattern' of calcification. The optical orientation of each biocrystal of *Oocardium* calcite is templated from the 'abiotic' crystals the initial *O. stratum* cells had settled on.

precipitation, but raises the question of to what extent abiotic precipitation may be speeded by biological mediation. Herein, for comparison, we take the calculated mean precipitation rates of flowstones in a half-cave next to a tufa waterfall (Boch, 2004) as representative of the rate of abiotic precipitation (A in Fig. 13). The comparison suggests that *Oocardium* calcification at Lingenau (B in Fig. 13) is more rapid by two to three orders of magnitude. This statement must however be viewed with caution. First, recall that the rate of *Oocardium* calcification is much lower at Alpenzoo and may not markedly exceed abiotic precipitation. Second, more comparative data from field-based precipitation experiments run over several years

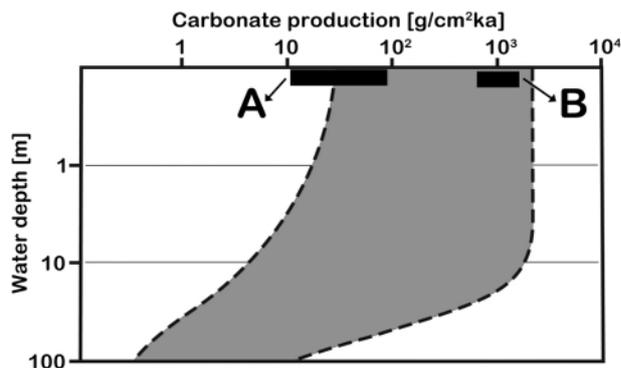


FIGURE 1 3: Comparison of rates of calcite precipitation. (A) Abiotic precipitation of flowstones within a halfcave adjacent to an active waterfall tufa (data from Boch, 2004). (B) Rate of precipitation of laminar *Oocardium* tufa at Lingenau, with annual lamina thickness ranging from 4 – 10 mm/a, and with 60% intrinsic porosity. Shaded area delimited by dashed line shows marine-tropical carbonate production rates relative to water depth (Sanders, 2003, modified from Enos, 1991). The thickness of black bars A and B does not realistically reflect the water depth of precipitation, but shall highlight the ranges of carbonate production. See text for further discussion.

and from a wider range of locations should be available to arrive at more definite results. Nevertheless, the rates indicated in Fig. 13 provide an impression of the potential biological speeding of calcium-carbonate deposition relative to abiotic precipitation. Wallner (1935b) observed that *Oocardium* can settle on plates of copper, provided that the plates became first encrusted by a thin lamina of calcite spar that seemed to have precipitated by abiotic processes. To judge from the scaled Figure 2 in Wallner (1935b, p. 38), the rate of calcification by *Oocardium* is higher by at least one order of magnitude than that of the abiotic calcite lamina. For active *Oocardium* tufas in the Schwäbische Alp (Germany), Wallner (1935c) had determined a growth rate of 5 mm/a; this is within the range determined by us for Lingenau.

At Alpenzoo, the calcification of *O. stratum* as botryoids and

(1) LINGENAU

Temperature [°C] at spring emergence	Electrical conductivity [uS/cm]	pH [-log(H ⁺)]	Ca [mg/l]	Mg [mg/l]	HCO ₃ ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	Other ions [mg/l]	Remarks
9.8–12.8° (6)	572–623 (6)	6.84–7.40 (6)	127 (avg 7)	4.6 (avg 7)	364 (avg 2)	7.9 (1)	Cl: 9.7 (1) Na: 5.5 (avg 2) K: 4 (avg 2) Si: 1.2 (1) Sr: 0.5 (1) Ba: 0.14 (1) Nitrate in micro-g/l: 2881 (1)	Most measurements taken from March 2005 to November 2005. Most data from Rüt (2006)

(2) ALPENZOO

Temperature [°C] at exit of spring capture	Electrical conductivity [uS/cm]	pH [-log(H ⁺)]	Ca [mg/l]	Mg [mg/l]	HCO ₃ ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	Other ions [mg/l]	Dissolved gases	Remarks
8.9–12.2° (7)	917–950 (7)	7.37–7.9 (7)	137 (1)	48 (1)	230 (2)	370 (1)	Cl: 5.7 (1) Na: 2.6 (1) K: 0.6 (1)	(a) O ₂ : 10.7 mg/l = 100% saturation (1) (b) CO ₂ : 14.5 mg/l = 37% saturation (1)	Measurements taken from April to October 2008

TABLE 2: Physico-chemical parameters of spring waters at Lingenau and Alpenzoo. The figure in parentheses behind each parameter indicates the number of times a parameter was measured. Numbers labelled 'avg' indicate average values. Numbers separated by hyphen indicate minimum-maximum ranges.

laterally-merged botryoids of ffC seems puzzling when seeking distinction from abiotically-formed ffC cement. The only hint on an origin of a botryoid of ffC in association with *Oocardium* is the presence of faint relicts of the 'tubes' left by the cells during their upward-shifting life (Fig. 11B – C). If it were not for these relicts, it would be hardly possible to distinguish the fascicular-fibrous form of *Oocardium* calcite from ffC cements grown under abiotic conditions (Fig. 11D – E). Among ancient marine reefs, buildups rich in cement prevailed at specific intervals of geological time (e. g. from Early Permian to Middle Triassic). The ancient 'cement reefs' show centimeter- to decimeter-sized patches of cementstone riddled by fossils (e. g. the interpreted red alga *Archaeolithoporella*, or the microproblematica *Tubiphytes* and *Ladinella*) that float within the cementstone. Whilst part of such textures may result from the effect of cutting through a three-dimensional reef framework, in many cement reefs the patches with bioconstructors floating cement seem so large and pervasive that these can hardly all be explained by the cutting effect. Our observations on the calcification of *O. stratum* raise the possibility that, in ancient cement reefs, some of the apparently abiotic cements originally had formed under biological mediation. Modeling of past changes in oceanic chemistry suggests that formation of cement reefs was favoured or perhaps triggered by elevated alkalinity of sea water (Tyrrell and Zeebe, 2004; Ridgwell, 2005), i. e. by conditions favourable for the microbially-induced type of biocalcification (Konhäuser, 2007). Furthermore, ancient seafloor-fringing cements interpreted to have formed by abiotic precipitation (Woods et al., 2007) in fact may have been started under biological mediation. In view of the extremely wide environmental range of potential microbial calcifiers, such as cyanobacteria or other bacteria (Schopf, 1999; Ehrlich, 2002), it indeed seems quite improbable that the formation of ancient seafloor precipitates proceeded in a strictly abiotic manner. From cold-spring limestones, Freytag and Verrechia (1999) described palisade fringes of columnar calcite crystals resulting from recrystallization of cyanobacterial mats which, in turn, originally calcified as micrite. Similar fabrics were observed by us in other deposits of spring-associated limestones of the Eastern Alps (Sanders et al., 2006a). Depending on water supply, and perhaps also on other factors such as alkalinity, the original microbial 'fingerprint' of an apparently abiotic cement fabric may therefore be largely wiped out. Today, aside from the cementstone produced by *O. stratum*, coarse-sparry calcite is produced by the cyanobacteria *Rivularia haematites* and *Phormidium foveolarum* (Janssen et al., 1999). The extent and crystal size (micrite to coarse spar) of *Rivularia* calcification correlate positively with the intensity of water supply (Sanders et al., 2006a, and unpubl. data), but the role of other factors such as water chemistry, photosynthesis, and possibly, organic substances on the style of cyanobacterial calcification is as yet hardly documented (Arp et al., 1999). It is in any case obvious that microbially-induced mineralization can be of widely variable style even for the same genus or species, and apparently abiotic

precipitates can be formed under microbial induction.

5. CONCLUSIONS

The desmid micro-alga *Oocardium stratum* (Zygnematophyceae) was identified in limestone-precipitating spring streams of the Eastern Alps. The alga calcifies in form of calcite, mainly during spring and summer over some 7–8 months per year. In late autumn, diatom mats spread directly on the *Oocardium* calcite. Thus, *Oocardium* tufa in many cases shows a lamination which is potentially related to seasonal changes of periphyton dominance. In colonization of pristine substrates, *O. stratum* seems to settle exclusively on pre-existing calcite crystals.

At Lingenau (Vorarlberg), spring limestones are formed almost exclusively by *O. stratum*, at rates of calcification between 4–8 mm per year. Calcification of *O. stratum* occurs in form of rhombohedral calcite precipitated as bush-shaped, single biocrystals up to about 8–10 mm in maximum observed height. In presence of copious water, the original *Oocardium* calcite rapidly transforms into a low-porous coarse-sparry calcite cementstone with only a few relict structures that hint on the microbial origin of 'first' calcification.

At Alpezenoo (Tyrol), *O. stratum* calcifies in botryoids and laterally-merged botryoids of fascicular-fibrous calcite (ffC). The *Oocardium* calcite of Lingenau and Alpezenoo differ in their growth style (laminar: Lingenau; botryoidal: Alpezenoo), habitus of calcite (rhombohedral calcite: Lingenau; ffC: Alpezenoo), and rate of calcification (rapid: Lingenau; slow: Alpezenoo). '*Oocardium calcite*' thus is not a single type of CaCO₃ precipitate.

The calcite habitus formed upon *Oocardium* biocalcification is controlled by the habitus of the abiotic calcite precipitate at site. A preliminary attempt to compare rates of abiotic calcite precipitation with *Oocardium* calcification suggests that the latter may be up to three orders of magnitude faster than abiotic precipitation.

Experimentally-determined rates of *Oocardium* calcification are comparable to high rates of marine tropical shallow-water carbonate production. The observations that botryoids and fringes of ffC can be induced by *O. stratum*, and that the formation of coarse-sparry cementstones can be started under microbial mediation, contributes to the argument that similar cements in ancient cement reefs and apparently abiotic seafloor precipitates of the geological past are of 'microbially-started' origin rather than representing strictly abiotic precipitates.

ACKNOWLEDGEMENTS

D. S. gratefully acknowledges financial support from project 'Kalktuff in Vorarlberg' funded by inatura Erlebnisschau Dornbirn. Rudolf Pavuza, Museum of Natural History, Vienna, is thanked for a constructive review. Helena Rodnight, University of Innsbruck, is thanked for a check of the English.

REFERENCES

- Amperfer, O., 1914. Über die Aufschliessung der Liegendmoräne unter der Höttinger Breckzie im östl. Weiherburggraben bei Innsbruck. Zeitschrift für Gletscherkunde, 8, 145-159.
- Arp, G., Thiel, V., Reimer, A., Michaelis, W. and Reitner, J., 1999. Biofilm expopolymers control microbialite formation at thermal springs discharging into the alkaline Pyramid Lake, Nevada, USA. Sedimentary Geology, 126, 159-176.
- Bathurst, R. C., 1975. Carbonate sediments and their diagenesis. Developments in Sedimentology, 12. Elsevier, Amsterdam, 658 pp.
- Berner, E. K. and Berner, R. A., 1996. Global Environment: Water, air, and geochemical cycles. Prentice-Hall, New Jersey, 376 pp.
- Boch, R., 2004. Untersuchungen an spät- und postglazialen Karbonaten Tirols. Unpubl. MS Thesis, University of Innsbruck, 122 pp.
- Chen, J., Zhang, D. D., Wang, S., Xiao, T. and Huang, R., 2004. Factors controlling tufa deposition in natural waters at waterfall sites. Sedimentary Geology, 166, 353-366.
- Ehrlich, H. L., 2002. Geomicrobiology. Marcel Dekker Inc., New York, 768 pp.
- Enos, P., 1991. Sedimentary parameters for computer modeling. In: E. K. Franseen, W. L. Watney, C. G. St. C. Kendall and W. Ross (eds.), Sedimentary modeling: Computer simulations and methods for improved parameter definition. Kansas Geological Survey Bulletin, 233, pp. 63-99.
- Ford, T. D. and Pedley, H. M., 1996. A review of tufa and travertine deposits of the world. Earth-Science Reviews, 41, 117-175.
- Freytet, P. and Verrecchia, E. P., 1998. Freshwater organisms that build stromatolites: a synopsis of biocrystallization by prokaryotic and eukaryotic algae. Sedimentology, 45, 535-563.
- Freytet, P. and Verrecchia, E. P., 1999. Calcitic radial palisadic fabric in freshwater stromatolites: diagenetic and recrystallized feature or physicochemical sinter crust? Sedimentary Geology, 126, 97-102.
- Golubic, S. and Marcenko, E., 1958. Zur Morphologie und Taxonomie der Desmidiaceengattung *Oocardium*. Schweizerische Zeitschrift für Hydrologie, 20, 177-185.
- Högl, O., 1980. Die Mineral- und Heilquellen der Schweiz. Verlag Paul Haupt, Bern und Stuttgart, 302 pp.
- Janssen, A., Swennen, R., Podoor, N. and Keppens, E., 1999. Biological and diagenetic influence in Recent and fossil tufa deposits from Belgium. Sedimentary Geology, 126, 75-95.
- Konhauser, K., 2007. Introduction to Geomicrobiology. Blackwell Publishing, Oxford, 425 pp.
- Lowenstam, H. A. and Weiner, S., 1989. On biomineralization. Oxford University Press, New York, 416 pp.
- Merz-Preiß, M. and Riding, R., 1999. Cyanobacterial tufa calcification in two freshwater streams: ambient environment, chemical thresholds and biological processes. Sedimentary Geology, 126, 103-124.
- Ostermann, M., 2006. Thorium-uranium age-dating of "impure" carbonate cements of selected Quaternary depositional systems of western Austria: results, implications, problems. Unpubl. PhD Thesis, University of Innsbruck, 173 pp.
- Paschinger, H., 1950. Morphologische Ergebnisse einer Analyse der Höttinger Breckzie bei Innsbruck. Schlern-Schriften, 75, 7-86.
- Patzelt, G. and Resch, W., 1986. Quartärgeologie des mittleren Tiroler Inntales zwischen Innsbruck und Baumkirchen. Jahresberichte und Mitteilungen der oberrheinischen geologischen Vereinigung, Neue Folge, 68, 43-66.
- Penck, A., 1921. Die Höttinger Breckzie und die Inntalterrasse nördlich Innsbruck. Abhandlungen der preussischen Akademie der Wissenschaften, physikalisch-mathematische Klasse, 1920, 1-136.
- Pentecost, A., 1991. A new and interesting site for the calcite-encrusted desmid *Oocardium stratum* Naeg. in the British Isles. British phycological Journal, 26, 297-301.
- Ridgwell, A., 2005. A Mid Mesozoic Revolution in the regulation of ocean chemistry. Marine Geology, 217, 339-357.
- Rüf, B., 2006. Quelltuff in Vorarlberg – Sedimentologische, materialkundliche und bauhistorische Aspekte. Unpubl. MS Thesis, University of Innsbruck, 173 pp.
- Sanders, D., 2001. Spring tufas and cemented slope deposits in gorges of the western Northern Calcareous Alps, Tyrol: an interim overview (abstr.). Geologisch-Paläontologische Mitteilungen Innsbruck, 25, 181-182.
- Sanders, D., 2003. Syndepositional dissolution of calcium carbonate in neritic carbonate environments: Geological recognition, processes, potential significance. Journal of African Earth Sciences, 36, 99-134.
- Sanders, D., 2008. Eislast-Erscheinungen und Intraklasten in der Höttinger Breckzie (Riß-Würm Interglazial) bei Innsbruck (Österreich). Geo.Alp, 5, 149-164.
- Sanders, D., Unterwurzacher, M. and Rüf, B., 2006a. Microbially-induced calcium carbonate in tufas of the western Eastern Alps: a first overview. Geo.Alp, 3, 167-189.
- Sanders, D., Krainer, K. and Unterwurzacher, M., 2006b. Geological controls on formation of tufa-precipitating spring (Eastern Alps): what do the maps tell? (abstr.). Innsbruck University Press, Conference Series, Pangeo 2006, pp. 291-292.

Sanders, D., Tessadri, R. and Rott, E., 2008. Quaternary spring-associated limestones of the Eastern Alps: implications for marine carbonates. *Geophysical Research Abstracts*, 10, EGU2008-A-02104.

Schopf, J. W., 1999. *Cradle of life. The discovery of Earth's earliest fossils*. Princeton University Press, Princeton, 367 pp.

Tucker, M. E. and Wright, V. P., 1990. *Carbonate Sedimentology*. Blackwell Scientific, Oxford, 482 pp.

Tyrrell, T. and Zeebe, R. E., 2004. History of carbonate ion concentration over the last 100 million years. *Geochimica et Cosmochimica Acta*, 68, 3521-3530.

Wallner, J., 1933. *Oocardium stratum* Naeg., eine wichtige tuffbildende Alge Südbayerns. *Planta*, 20, 287-293.

Wallner, J., 1934a. Ueber die Beteiligung kalkablagernder Pflanzen bei der Bildung südbayerischer Tuffe. *Bibliotheca Botanica*, 110, 1-30.

Wallner, J., 1934b. Über die Verbreitungsökologie des Desmidiacee *Oocardium*. *Planta*, 23, 249-263.

Wallner, J., 1935a. Zur Kenntnis der Gattung *Oocardium*. *Hedwigia*, 75, 130-136.

Wallner, J., 1935b. Eine Süßwasseralge besiedelt metallisches Kupfer. Beihefte zum Botanischen Centralblatt, 53, Abteilung A, 591-594.

Wallner, J., 1935c. Eine gesteinsbildende Süßwasser-Alge Deutschlands. *Natur und Volk*, 66, 85-91.

Willegger, C., 2008. Biokalzifikation der Grünalge *Oocardium stratum*. Unpubl. BS Thesis, University of Innsbruck, 39 pp.

Woods, A. D., Bottjer, D. J. and Corsetti, F. A., 2007. Calcium carbonate seafloor precipitates from the outer shelf to slope facies of the Lower Triassic (Smithian-Spathian) Union Wash Formation, California, USA: Sedimentology and paleobiologic significance. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 252, 281-290.

Zötl, J. and Goldbrunner, J. E. (eds.), 1993. *Die Mineral- und Heilwässer Österreichs – Geologische Grundlagen und Spurenelemente*. Springer, Vienna, 324 pp.

Received: 27. October 2008

Accepted: 10. March 2009

Diethard SANDERS¹⁾ & Eugen ROTT²⁾

¹⁾ Institute of Geology and Palaeontology, Faculty of Geo- and Atmospheric Sciences, University of Innsbruck, Innrain 52, 6020 Innsbruck, Austria.

²⁾ Institute of Botany, Faculty of Biology, University of Innsbruck, Sternwartestraße 15, 6020 Innsbruck, Austria.

³⁾ Corresponding author, diethard.g.sanders@uibk.ac.at